Non-Magnetic Corrosion Resistant High Strength Steels

This invention relates to non-magnetic corrosion resistant high strength steels. More especially, but not exclusively, the invention relates to steels suitable for use as non-magnetic components in directional drilling of oil and gas wells.

When deep well drilling, long tubular drill collars are located at the lower ends of drill strings to provide weight and rigidity. Lengths of these collars are typically between 1 and 10 metres and their diameters are typically between 8.75 and 32.5cm. Each such collar includes a central, axial hole of diameter typically between 5.75 to 12.75 cm which allows drilling fluid to pass down the string to the well base. This fluid subsequently, returns to the surface outside the drill collar and string. Threaded ends allow the collars to be secured to one another and to other components of the string. Dimensional and mechanical property requirements are laid down in API 7 Section 6.

It is often desirable to include instruments near the bottom of the drill string to enable the angle and direction of drilling to be measured accurately. The proximity of a large ferromagnetic mass is such instruments is clearly undesirable. When instruments are to be employed, low alloy steels conventionally used for the manufacture of drill collars have been replaced

with steels having low magnetic permeability. Precipitation hardened nickel-copper alloys and special austenitic stainless steels have been used previously as replacement steels. The strength requirements for drill collars (typically 0.2% proof strength in excess of 100 ksi (690 mPa)) cannot be achieved with a nickel copper alloy or with standard chromium nickel steels of the '300' series even when annealed, and while such steels can be strengthened by cold straining, the degree of deformation required is prohibitive, especially in the large sections involved. Moreover, some standard nickel chromium steels have austenitic structures of limited stability and can have their magnetic permeability increased by deformation. Consequently, a series of special steel grades was developed for this specialised application, these having analyses typified by steels A and B below:

	C	Si	Mn	Cr	Ni	Mo	N
A	.05	.5	18	13	2.3	.5	.3
B	.03	.5	10	18	7	-	.35
C	.03	.4	19	16.5	.7	-	.5

In these steels, yield strength is increased by the presence of relatively high nitrogen contents. This presence also increases strain - hardening rate, as does the reduction in nickel content. The relatively high manganese levels are necessary to retain the high nitrogen contents during normal melting, casting and solidification at atmospheric pressure, and also to improve the stability of the austenitic structure. A low carbon content is necessary to limit the formation of chromium rich carbides during processing; the presence of such carbides can adversely reduce resistance to corrosion. Even with these special steels, some strain hardening is necessary to generate the required strength. This can, however, be readily achieved, even in the largest sections, by deformation at temperatures below

that which produces auto-recrystallisation.

Steels A and B therefore provided the required yield strength, but at the expense of other desired properties.

Of the desired properties, low magnetic permeability is paramount and the alloying balance must be such that the structure is both free from delta ferrite and will not be destabilised by deformation. A number of methods have been proposed by which the structure of a steel may be predicted from its composition. These all involved separating the elements into those which act similarly to chromium and those similarly to nickel. Each was allocated an equivalence factor and by means of these the total chromium equivalence and nickel equivalence are calculated. The interceptor of these two values on a diagram is reported to show structure including some indication of the proportions of phases in a multi-phase case. The diagrams are used with some success within certain composition ranges but have proved less successful elsewhere. One obvious inaccuracy is that the same equivalence values are used whether austenite-ferrite boundaries or austenite martensite boundaries are being predicted, which cannot be the case.

A hazard with all steels used in drill strings is galling at the threaded joints. Such joints must be made at high torques to minimise stress concentration in service and provide effective seals at mating shoulders. In this context, galling may be described as localised friction-welding of surfaces moving relative to one another under pressure. Galling can prevent successful jointing of components and/or prevent release of the joint between components after use. The damage caused on thread and shoulder surfaces (production of cavities and metal build up) can render them unsuitable for further use and, although some re-threading can be achieved, the lives of the components are shortened. Austenitic stainless steels are especially prone to galling and, although compositions A and B are superior

in this respect to more conventional 300 series stainless steels, improved galling resistance was required which led to the development of composition C. This composition is now widely used.

A further service hazard is that of corrosion. Drilling fluids used are commonly aqueous and compositions are chosen to be compatible with the strata being drilled. Drilling fluids often have large contents of solids, both soluble and insoluble, notably chlorides and, less frequently, bromides which can cause corrosion problems. To minimise this, pH is usually kept above neutral so that hydrogen evaluation cannot be a corrosion product, and the cathodic corrosion reaction will normally involve water and dissolved oxygen producing the hydroxyl ion. Thus the availability of dissolved oxygen will control the rate of corrosion possible; because the source of oxygen is the atmosphere, dissolved oxygen of the fluid will be controlled by drilling conditions and procedures. It is usually low enough for there to be few problems with low alloy steel components. With these, any corrosion is general in nature and therefore, with limited oxygen availability the resulting general charges in dimension are small and tolerable.

Corrosion of stainless steels in more alkaline solutions does not occur because of the presence of a stable oxide film on the surface (the passive film). In the presence of certain dissolved salts, and notably chlorides and bromides, this film can fail locally allowing the production of "pits". Although total corrosion rate is slower than for a low alloy steel in the same environment, the local penetration can be more rapid. such film breakdown is more likely within crevices where it can spread to be general within the confines of the crevice. Oxygen is necessary for such corrosion to initiate and propagate and probability is more likely with higher contents of chloride and/or bromide and oxygen. Probability is also greater at height temperatures as can apply downhole. Thus some corrosion is possible with the non-magnetic steels depending upon service conditions but, with collars, this has rarely been of consequence, the pits being of limited size and

occurring in large sections.

Localised corrosion can be of more consequence in the non-magnetic steel casings used to contain the sophisticated electronic measuring devices used when drilling. The internal geometry within these devices can be complex and involve functional crevices and also changes in section, which can retain deposits, producing crevices. In these elaborate devices, localised corrosion is less tolerable than for the relatively simple collars. Furthermore, there can be a mixture of metals in electronic contact which can exacerbate conditions by galvanic effects. Thus there is need for a steel of enhanced resistance to localised corrosion which exhibits the other desired properties mentioned previously, these being high strength, low magnetic permeability, structural stability and anti galling properties.

None of the previously discussed steels provide all these desired properties.

The invention sets out to provide such a steel which does have all of these desired properties.

According to the present invention in one aspect, there is provided a non-magnetic corrosion resistant high strength steel whose composition by weight % includes:-

Carbon,	up to 0.05%
Silicon,	up to 1.0%
Manganese,	from 10.0 to 20.0%
Chromium,	from 13.5 to 18.0%
Nickel,	from 1.0 to 4.0%
Molybdenum,	from 1.5 to 3.5%
Nitrogen,	from 0.2 to 0.4%

In another aspect, the invention provides a non-magnetic corrosion and galling resistant high strength steels whose composition by weight includes

Carbon	up to 0.2%
Silicon	up to 1.0%
Manganese	from 10.0 to 20.0%
Chromium	from 13.5 to 18.0%
Nickel	from 1.0 to 7.0%
Molybdenum	from 1.5 to 4.0%; and
Nitrogen	from 0.2 to 0.4%,

the composition satisfying the formulae:-

(i) $\frac{\text{Nickel equivalence}}{\text{Chromium equivalence minus 14}} > 1.51$

and

(ii) Nickel equivalence + chromium equivalence > 35

A preferred composition by weight % of steels in accordance with the invention is carbon up to 0.55%, silicon up to 1%, manganese 12 to 16%, chromium 14 to 16%, nickel 1.0 to 5%, molybdenum 1.7 to 3.0% and nitrogen, 0.2 to 0.40%, balance iron and incidental impurities.

A further more limited composition by weight % is carbon up to 0.035%, silicon up to 0.5%, manganese 13 to 15.0%, chromium 15 to 16%, nickel 2.0 to 2.75%, molybdenum 2.0 to 2.5% and nitrogen 0.30 to 0.40%, balance iron and incidental impurities.

Preferably, the balance of the composition conforms with the following equation:-

$$\frac{\text{Ni equivalence}}{\text{Cr equivalence - 14}} > 1.51$$

when Cr equivalence = %Cr + 1.5% Si + %Mo + 0.12% Mn

and

Ni equivalence = %Ni + 30%C + 20% N

Additionally, the balance of the composition may conform with the following equations :

Cr equivalence = Cr + 1.5% Si + % Mo + 0.12% Mn

and

Ni equivalence = %Ni + 30% C + 20% N

and

Ni equivalence + Cr equivalence > 35.

where Cr equivalence = % Cr + 1.5% Si + %Mo; and

Ni equivalence = % Ni + 0.5% Mn + 30% C + 30% N.

In another aspect, the invention provides a non-magnetic component for use in directional drilling produced from a nigh strength corrosion resistant steel of composition as specified in any one of the preceding four paragraphs. The component may be a drill collar.

It is well known than an essential component of a stainless steel is chromium, at least 12% by weight in solid solution being generally deemed to be desirable. For the type of corrosion in question (caused by dissolved halide salts), increasing the content of chromium above this value progressively improves resistance to corrosion initiation and its rate of propagation. A number of other elements can complement the beneficial effect of chromium, notably molybdenum. Both chromium and molybdenum however, promote the formation of magnetic delta ferrite phase which cannot be tolerated for the particular use under consideration. To prevent the presence of this ferrite phase, there must be present in sufficient amounts elements which suppress its formation, notably carbon, nickel and nitrogen. The tolerable content of carbon is very low because the presence

of carbides can be deleterious to corrosion resistance. Nickel has a deleterious effect on the tendency for galling and thus its content must also be low. Nitrogen, however, has no deleterious effect on galling and, moreover, in the presence of chromium, improves resistance to corrosion. However, the quantity of nitrogen which can be retained in a steel on freezing is limited unless there is sufficient appropriate alloying of the current type. While chromium promotes solubility in proportion to its content, chromium alloying alone is insufficient and it has to be supplemented with manganese. Manganese, however, adversely effects resistance to corrosion.

A very careful balance of alloying is therefore necessary if the required downhole property balance of the steel is to be achieved.

As mentioned previously, of the desired properties, low magnetic permeability is paramount and the alloying balance must be such that the structure is both free from delta ferrite and will not be destabilised by deformation. A number of methods have been proposed by which the structure of a steel may be predicted from its composition. These all involved separating the elements into those which act similarly to chromium and those similarly chromium and those similarly to nickel. Each was allocated an equivalence factor and by means of these the total chromium equivalence and nickel equivalence are calculated. The interceptor of these two values on a diagram is reported to show structure including some indication of the proportions of phases in a multi-phase case. The diagrams are used with some success within certain composition ranges but have proved less successful elsewhere. One obvious inaccuracy is that the same equivalence values are used whether austenite-ferrite boundaries or austenite martensite boundaries are being predicted, which cannot be the case. For the present invention the factors used for the two aspects are not necessarily the same as published and the approach has been simplified by using a simple equation to predict whether or not ferrite is present and the sum of factors to indicate a suitable austenite stability. It is not believed

that the various factors used will necessarily apply to other alloy mixes other than the range relevant to this invention.

Applicants has established that an excellent downhole property balance is achieved with high strength corrosion resistant steels having the following composition by weight:-

Carbon	Up to 0.05%
Silicon	Up to 1.0%
Manganese	10 to 20%
Chromium	13.5 to 18%
Nickel	1.0 to 7.0%
Molybdenum	1.0 to 4.0%
Nitrogen	0.2 to 0.4%

In addition, it is preferred that the balance of composition conforms with the following:-

With $\frac{\text{Nickel equivalence}}{\text{Chromium equivalence minus 14}} > 1.51$

Where chromium equivalence = % chromium + 1.5 x % silicon + % molybdenum + 0.12 x % manganese and nickel equivalence = % nickel + 30 x % carbon + 20 x % nitrogen and also with nickel equivalence + chromium equivalence >35.

Where chromium equivalence = % chromium + 1.5 x % silicon + % molybdenum and nickel equivalence = % nickel + 0.5 x % carbon + 30 % nitrogen.

All the above values are percentages by weight with the balance essentially iron. It is to be understood that the elements normally incidentally present in austenitic stainless steels may be present within the

limits set for such steels in BS970 Part 1. Preferred and more preferred compositions are as follows.

	Preferred	More Preferred
Carbon	.05% maximum	.035% maximum
Silicon	1.0% maximum	.50%
Manganese	12.0 to 16.0%	13.0 to 15.0%
Chromium	14.0 to 16.0%	15.0 to 16.0%
Nickel	1.0 to 5.0%	2.0 to 2.75%
Molybdenum	1.7 to 3.0%	2.0 to 2.5%
Nitrogen	.20 to .40%	.30 to .40%

It is to be understood that the elements normally present as incidentals in stainless steels may also be present in the quantities normally accepted in international standards.

One example of a steel composition in accordance with the invention is:

C	Si	Mn	Cr	Ni	Mo	N
0.031	0.50	14.86	15.06	2.46	2.02	0.30

This steel was forged to form 10 metre length bars of 180 mm and 190 mm diameter by a normal production technique including hot forging and warm straining. The mechanical properties taken from positions in accordance with API 7 Section 6 were:

0.2% Proof Stress	118.9 ksi (MPa)
U.T.S.	139.9 KSI (MPa)
Elongation	37%
Reduction of Area	68%
Charpy 'V' (20°)	156, 164, 167 Joules

Magnetic permeability was 1.002 and uniformity of this property was confirmed by measuring the changing magnetic flux along the bar when subjected to a magnetic force of 200 oersteds. Maximum deviation was found to be less than 0.05 micro tesla over the whole bar length.

Resistance to galling was demonstrated by use of the button-on-block technique described in ASTM G98. This involves rotating separate cylindrical samples under pressure on blocks of similar material. Increasing pressures being used until galling is seen. Results are compared with those for steels A to B and C in Table 1 below.

TABLE 1

Pressure, ksi	Steel A	Steel B	Steel C	Steel of the present Invention
3.5		Not galled		
6.5		Not galled		
9.5		Not galled		
10	Not Galled	Galled		
12	Not Galled	Galled		
14	Not Galled	Galled		
15	Not galled			
17.5	Not galled			
20	Galled		Not galled	Not galled
25			Not galled	Not galled
30			Not galled	Not galled
32.5			Not galled	Not galled
35			Not galled	Not galled
36.25			Galled	Not galled
37.5			Galled	Not galled
40				Not galled
42.5				Not galled

It will be seen from this Table that steel B galled at around 10 ksi, steel A at around 20 ksi and steel C at around 36.25. The steel sample in accordance with the invention had not galled at the highest recorded pressure, namely 42.5 ksi.

Corrosion resistance was demonstrated by two accelerated laboratory tests. The corrodent chosen was a 20% solution of sodium chloride at 50°C open to atmosphere. The test sample was a small cylinder and this was embedded in a layer of fine sand to simulate severe crevice conditions. The sample was connected via an ammeter to an electrode either of copper or of type 304 stainless steel; the electrode surface area was 150 sq cms. The current flow provided an indication of the corrosion occurring. To accelerate the test there was an initial period when the test sample was polarised anodically at a high current to ensure that corrosion had started and was proceeding at a high rate. After stopping polarisation, the current flow was monitored until a steady value was obtained and this was noted. Values for static and flowing solutions were taken. These are tabulated in Table 2 below:-

TABLE 2

	Copper Electrode		304 Electrode	
	Static	**Flowing**	**Static**	**Flowing**
	mA	mA	mA	mA
Steel A	4.9	6.4	2.1	2.7
Steel C	4.4	6.8	2.2	3.4
Steel of the present invention	0.33	0.15	0.50	0.79

The test with the stainless steel electrode simulated severe crevice conditions and that with the copper electrode the added effect of galvanic stimulation. It will be seen from Table 2 that the steel sample of the present

invention exhibited substantially enhanced corrosion resistance.

The tests conducted demonstrated that steels in accordance with the present invention exhibit a property balance for strength, magnetic permeability, galling resistance and corrosion resistance superior in every respect to presently available high strength corrosion resistant steels.

It will be appreciated that the foregoing is merely exemplary of non-magnetic corrosion resistant high strength steels and non-magnetic components produced therefrom in accordance with the invention and that various modifications can be made thereto without departing from the true scope of the invention.

This Sheet Has Been Replaced





CLAIMS

1. A non-magnetic corrosion resistant high strength steel whose composition by weight % includes:-

Carbon,	up to 0.05%
Silicon,	up to 1.0%
Manganese,	from 10.0 to 20.0%
Chromium,	from 13.5 to 18.0%
Nickel,	from 1.0 to 4.0%
Molybdenum,	from 1.5 to 3.5%
Nitrogen,	from 0.2 to 0.4%

2. A non-magnetic corrosion and galling resistant high strength steel whose composition by weight includes

Carbon	up to 0.2%
Silicon	up to 1.0%
Manganese	from 10.0 to 20.0%
Chromium	from 13.5 to 18.0%
Nickel	from 1.0 to 7.0%
Molybdenum	from 1.5 to 4.0%; and
Nitrogen	from 0.2 to 0.4%,

the composition satisfying the formulae:-

(i) $\frac{\text{Nickel equivalence}}{\text{Chromium equivalence minus 14}} > 1.51$

and

(ii) Nickel equivalence + chromium equivalence > 35

3. A steel as claimed in claim 1 or claim 2 whose composition by weight

This Sheet Has Been Replaced



% is carbon up to 0.55%, silicon up to 1%, manganese 12 to 16%, chromium 14 to 16%, nickel 1.0 to 5%, molybdenum 1.7 to 3.0% and nitrogen, 0.2 to 0.40%, balance iron and incidental impurities.

4. A steel as claimed in claim 1 or claim 2 whose composition by weight % is carbon up to 0.035%, silicon up to 0.5%, manganese 13 to 15.0%, chromium 15 to 16%, nickel 2.0 to 2.75%, molybdenum 2.0 to 2.5% and nitrogen 0.30 to 0.40%, balance iron and incidental impurities.

5. A steel as claimed in any one of claims 1 to 4 wherein the balance of the composition conforms with the following equation:-

$$\frac{\text{Ni equivalence}}{\text{Cr equivalence} - 14} > 1.51$$

* C L M S *

when Cr equivalence = %Cr + 1.5% Si + %Mo + 0.12% Mn

and

Ni equivalence = %Ni + 30%C + 20% N

6. A steel as claimed in claim 5 wherein the balance of the composition conforms with the following equations :

Cr equivalence = Cr + 1.5% Si + % Mo + 0.12% Mn

and

Ni equivalence = %Ni + 30% C + 20% N

and

Ni equivalence + Cr equivalence > 35.

where Cr equivalence = % Cr + 1.5% Si + %Mo; and

Ni equivalence = % Ni + 0.5% Mn + 30% C + 30% N.

7. A non-magnetic component for use in directional drilling produced from a high strength corrosion resistant steel of composition as claimed in

This Sheet Has Been Replaced