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(54) IMPROVEMENTS IN OR RELATING TO HIGH STRENGTH STEELS

(71) We, OVAKO OY, a Finnish body corporate of 55100 Imatra 10, Finland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

- 5 The present invention relates to high strength steel. 5
 In order to increase the lifetime of machine parts by preventing corrosion, many different method are known in which the parts are coated with a protective layer. One such method is diffusion chromizing.
 10 According to the present invention there is provided steel comprising from 0.01 wt% to 0.08 wt% carbon, from 0.1 wt% to 1.0 wt% silicon, from 0.5 wt% to 2.2 wt% manganese, 10
 from 2.0 wt% to 10.0 wt% chromium, from 0.01 wt% to 0.4 wt% molybdenum, from 0.001 wt% to 0.05 wt% aluminium (acid soluble) and at least one of the carbide forming elements, titanium, zirconium, niobium and tantalum, so that the content of the carbide forming elements is more than 0.1 wt%, not more than 1.0 wt%, and wherein the balance 15
 of the steel is iron together with normal impurities.
 Steels of this composition are particularly suitable for treatment by diffusion chromizing and have quenched mechanical properties corresponding to those of quenched and 20
 tempered machine construction steels. Diffusion chromizing is accomplished by maintaining the part to be coated at a temperature above 900°C in an atmosphere containing chromium atoms, e.g. some chromium halide, usually chromium chloride (CrCl₂). 20
 Chromium atoms from the chromium chloride are transferred to the surface of the part to be chromized where they displace iron atoms from the surface in a so-called exchange reaction.
 25 A chromium rich zone is thus produced at the surface of the iron, from which chromium diffuses inwards. The chromium potential of the atmosphere is usually between 40--60 wt%. An α -ferrite zone is first formed at the surface of the part. The thickness of that zone increases at the same rate as chromium diffuses inwards until its content exceeds about 11 wt% (at 1100°C). This can be seen from the Fe-Cr-phase diagram represented in Figure 1, 25
 where the isotherm (1) at 1100°C is drawn. The curved lines 2, 3 are the calculated phase boundaries of α - and γ -phases respectively. Experimental values obtained by the following 30
 methods are also shown on the figures.
 35
 ◊ Adcock (thermal)
 ◆ Bungardt et al (dilatometric)
 o Nishizawa (micro probe) 35

The figures in brackets in Figure 1 correspond to the wt% chromium content where

$$\text{wt\% Cr} = \frac{\text{atom \% Cr} \cdot A_{\text{Cr}}}{(100 - \text{atom \% Cr}) \cdot A_{\text{Fe}} + \text{atom \% Cr} \cdot A_{\text{Cr}}} \quad 5$$

wherein A_{Fe} = atomic wt of iron
and A_{Cr} = atomic wt of chromium.

The formation of α -ferrite starts, when the chromium content exceeds the value corresponding to the intersection of the isotherm and the ν -(ν + α) phase boundary 2, this value being 11 wt% at 1100°C. The microstructure is totally α -ferritic at all temperatures when the chromium content exceeds 13.2 wt%. The thickness of the diffusion chromized zone is such that a portion of the zone contains at least 12 wt% chromium and the metal has been transformed to α -ferrite during chromizing. Hence no separate layer is formed on the surface of the part as in electrolytic surface treatments or in molten metal dipping treatments, but the protective zone forms in the metal itself by diffusion of chromium from the surface inwards.

The growth rate of the diffusion zone during diffusion chromizing depends on the following parameters: chromium potential of the chromizing agent, diffusion rate of chromium in ferrite, chromium content of the steel and chromium content corresponding to the austenite-ferrite phase transformation.

The most important requirement for a steel which is to be subjected to diffusion chromizing is a very low carbon content in order to avoid the formation of a carbide barrier under the surface which would hinder the chromium diffusion. The low carbon content can be attained either by lowering the carbon in the oxidising stage of steelmaking process to a sufficient low level or by stabilizing free carbon with carbide formers.

In order to attain good mechanical properties the hardenability of the steel must be adequate, i.e. the steel must be properly alloyed.

Steels embodying the invention will now be particularly described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is a Fe - Cr phase diagram;

Figure 2 is a graph showing the effect of various metals on the chromium diffusion time of steel; and

Figure 3 is a graph of chromium distribution after chromium diffusion.

These steels contain a combination of alloying elements which have been selected to give the steel a good hardenability. The steel has been alloyed mainly with a ferrite stabilizing element, chromium (Cr), which causes the diffusion chromizing time required to attain a certain coating thickness to be considerably shorter than with steels alloyed mainly with austenite stabilizing elements like manganese or nickel.

Account has been taken of the fact that the transfer rate of the ferrite-austenite phase boundary, which can be considered equal to the growing rate of the diffusion zone thickness, depends on the chromium content of the steel and on the relative stability of austenite in comparison to the ferrite at the diffusion chromizing temperature.

Manganese and nickel widen the austenite stability range and accordingly raise the chromium content corresponding to the austenite-ferrite phase transformation. Because the diffusion rate of chromium in austenite is significantly smaller than in ferrite, the austenite stabilizing elements tend to retard the progress of the phase boundary and hence the growth of the diffusion zone compared to unalloyed steels. Correspondingly, the chromium content of steel decreases that amount of chromium which has to be diffused into the austenite before the austenite-ferrite phase transformation can take place, thus increasing the growth rate of the diffusion zone compared to an unalloyed steel.

The effect of alloying on the diffusion zone growth rate has been investigated mathematically, using known diffusion equations, diffusion rate coefficients and phase diagrams. The results obtained by calculations have been confirmed by diffusion chromizing experiments carried out on various alloyed steel specimens. The calculated and experimental results are presented in Figure 2. The vertical scale of the graph represents the time in hours needed to obtain a 100 μ m thick diffusion zone at a temperature of 1100°C using a chromizing agent with a chromium potential of 40 wt% Cr. The horizontal scale represents the content of the main alloying element in the steel (Cr, Mn or Ni).

The curves drawn in Figure 2 indicate the calculated effects of nickel, manganese and chromium on the chromizing time. From these curves it can be seen that steel containing 2 wt% Nickel has a calculated chromizing time approximately 95% longer than a steel containing 4 wt% chromium. The experimental results obtained with differently alloyed steel specimens were reduced to correspond to a diffusion zone thickness of 100 μ m and are

presented in the same figure. The composition of the steel specimens was as follows:-

- 5 \triangle Armco iron
 \square 3,67 Wt% Ni, 0,41 Wt% Mn
 \circ 0,06 Wt% Ni, 3,70 Wt% Mn, 0,09 Wt% Cr
 \times 0,29 Wt% Ni, 0,93 Wt% Mn, 4,53 Wt% Cr
 $+$ 0,09 Wt% Ni, 0,52 Wt% Mn, 9,9 Wt% Cr.
- 10 The carbon content of all steel specimens used in the experiments was about 0.05% C and
 the niobium content about 0.08% Nb. The amounts of other alloying elements are indicated
 in figure 2. The calculated and experimental results have a fair correlation. Further
 calculations, based on a chromizing process giving a 100 μ m thick diffusion zone at the
 temperature of 1100°C and with the chromizing agent with a chromium potential of 40% wt
 Cr give that per one percent by weight of alloying element, manganese increases the
 15 chromizing time by about 2 to 3%, nickel increases it by about 19%, but chromium
 decreases the chromizing time by about 6%.
- 20 The time saving is of great significance because normal chromizing times are rather long.
 The carbon content of the steel is preferably from 0.01 to 0.05 wt% whereas the preferred
 amount of manganese is from 0.5 to 1.0 wt%. The preferred range for the chromium
 content is from 4.0 to 8.0 wt%.
- 25 The amount of residual elements and impurities present in the steels corresponds to the
 requirements set up for high quality machine construction steels. The lower limit of the
 carbon content is determined by sufficient hardness of the martensite and by the diffusion
 chromizing and corrosion properties. The effect of chromium on the chromizing time is
 small at the lower limit (2%). At the upper limit (10%) the steel has a high hardenability
 and superior diffusion chromizing and corrosion properties.
- 30 The corrosion resistance especially in cases when the chromized surface may get
 scratched is better the higher the chromium content of the base material. Since steel must
 be wholly austenitic, i.e. in the γ phase prior to hardening, the hardening temperature will
 increase drastically if the chromium content exceeds about 10 wt%, as can be seen from
 figure 1 where the $\gamma - (\gamma + \alpha)$ phase boundary 2 rises steeply after about 10 wt% chromium.
 Particularly preferable is the chromium content range from 4.0 wt% to 8.0 wt%. This range
 results in a good hardenability and growth rate of the diffusion zone and hardening
 temperature is low. However, the hardenability is not too high to prevent getting a
 favourable soft microstructure for e.g. cold forming by a suitable cooling.
- 35 There follows the results of diffusion chromizing experiments that have been carried out
 on steels. The chemical analyses of the steels used are presented in Table 1.

TABLE 1.

The analyses of the experimental steels in wt-%.

Steel	C	Si	Mn	Cr	Ni	Mo	Cu	V	Ti	Nb	Zr	Al _{sol.}
A	0.016	0.00	0.00	0.01	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.010
B	0.052	0.27	0.67	4.05	0.18	0.04	0.19	0.01	0.01	0.227	0.00	0.030
C	0.060	0.25	0.93	4.53	0.29	0.04	0.17	0.01	0.01	0.10	0.00	0.016
D	0.040	0.17	0.79	4.02	0.14	0.02	0.15	0.00	0.01	0.11	0.00	0.010
E	0.070	0.26	0.64	6.4	0.08	0.02	0.03	0.02	0.01	0.10	0.00	0.002
F	0.050	0.19	1.28	7.9	0.08	0.20	0.03	0.02	0.01	0.03	0.16	0.002
G	0.050	0.79	1.24	3.3	0.08	0.04	0.03	0.02	0.01	0.20	0.00	0.003
H	0.031	0.34	0.87	5.5	0.08	0.33	0.03	0.02	0.01	0.55	0.17	0.004
I	0.060	0.13	0.52	9.9	0.09	0.04	0.03	0.03	0.01	0.10	0.00	0.009
J	0.051	0.53	1.88	3.9	0.16	0.05	0.21	0.03	0.10	0.09	0.00	0.004
K	0.073	0.32	0.95	7.2	0.18	0.04	0.20	0.03	0.18	0.31	0.00	0.008

Steel A is Armco iron used for comparison. Diffusion chromizing experiments were carried out using a powder pack method on steels A, B and C and using a carrier gas method on steels C--K. In the powder pack method the parts to be chromized were packed in chromizing powder. The composition of the powder was the following:

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50 wt% Cr-powder (grain size 60 mesh)
45 wt% Al_2O_3 -powder
5 wt% NH_4Cl

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10 The chromizing temperature was 1100°C. In the carrier gas method the specimen to be chromized and chromium powder were placed in a tube furnace, which was heated to a temperature of 1100°C. Hydrogen saturated with hydrochloric acid was passed through the furnace in such a way that the gas mixture first contacted the chromium powder and then the specimen. A reaction occurred between the hydrochloric acid in the gas mixture and the chromium powder producing chromous chloride which then gave up its chromium atom to the surface of the steel specimen via the exchange reaction. Results of these diffusion chromizing experiments are presented in tables 2--3.

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TABLE 2.

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Results of the diffusion chromizing experiments with powder pack method

Steel	Zone thickness, μm	Time, h
25 A	75	4
A	176	12
B	83	4
30 B	161	8
B	208	12
35 C	86	4
C	146	8
C	195	12
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TABLE 3

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Results of the diffusion chromizing experiments with carrier gas method (1100 C, 5 h).

Steel	C	D	E	F	G	H	I	J	K
Zone thickness (μm)	115	110	130	145	110	125	170	110	135

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Results show that the growth rate in the steel of the invention is faster than that in the comparison steel A. Figure 3 shows two chromium distribution curves in diffusion zones obtained in chromizing experiments. According to the measurements the chromium content on the surface varies between 40 and 60 wt%.

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In table 4 are presented the results of the tensile tests of specimen which are diffusion chromized with powder pack method (steels B and C):

TABLE 4

Results of the tensile and hardness tests carried out with diffusion chromized specimen (powder pack method).

5	Steel/ chromizing time, h	Yield strength N/mm ²	Tensile strength N/mm ²	Elongation of rupture %	Reduction in area %	Hardness HV 10	5
10	B/4	560	760	14.8	65.8	253(385)	10
	C/4	610	880	14.6	65.9	302(367)	
	B/12	510	660	18.0	68.6	239(302)	
	C/12	590	740	16.0	74.0	258(376)	
15	The mechanical properties were for tensile test specimens which had been cooled in the chromizing box for 1/2 hour from 1100°C to near room temperature. The hardness values in the parenthesis were for test specimen quenched in water. Chromized surfaces were faultless after quenching. Therefore it was found that water quenching was preferable for the steels.						15
20	Table 5 shows the results of the tensile tests of the steels E--K after simulated chromizing and tempering for 1 hour at 450°C. The simulation was carried out by annealing the specimen for 5 hours at 1100°C in an oxygen free atmosphere and cooling in air.						20
25	Table 6 shows the results of the tensile tests of steels C--K after simulated diffusion chromizing and austenising for 1/2 hour at 920°C, water quenching and tempering (1 h) if indicated.						25

TABLE 5

30 *Results of the tensile and hardness tests after simulated chromizing (1100°C, 5h) and cooling in air plus tempering (450°C, 1h).*

Steel	Yield Strength, N/mm ²	Tensile strength, N/mm ²	Elongation of rupture %	Reduction in areas %
E	903	981	14.9	65.8
F	1005	1084	13.7	66.5
G	814	952	15.9	64.5
H	667	716	15.3	64.3
I	1020	1168	16.6	59.8
J	957	1104	15.3	62.7
K	1035	1153	14.2	61.8

TABLE 6

Results of the tensile tests after simulated chromizing (1100°C, 5 h) and cooling in air, plus austenising (920°C, 1/2 h), water quenching plus tempering (1 h) if indicated.

5		Tempering	Yield strength,	Tensile strength,	Elongation of rupture	Reduction in area	5
10		°C	N/mm ²	N/mm ²	%	%	10
10	C	none	820	995	12.0	67.5	
	C	500	855	990	14.8	70.5	
15	D	none	815	1030	14.6	74.3	15
	D	450	885	1000	16.0	75.8	
20	E	none	947	971	13.4	70.0	20
	E	450	839	952	16.5	65.5	
	F	none	1005	1040	14.5	66.5	
25	F	450	873	1025	15.8	65.8	25
	G	none	1001	1060	13.0	67.8	
30	G	450	883	1020	17.4	68.5	30
	H	none	628	662	15.7	68.8	
	H	450	569	647	17.0	71.2	
35	I	none	972	1143	11.5	56.5	35
	I	450	957	1118	17.0	65.5	
40	J	none	1065	1109	13.6	65.7	40
	J	450	971	1089	16.3	67.0	
	K	none	972	1109	12.2	61.8	
45	K	450	961	1089	14.7	72.5	45

The experimental results show that these steels are very well suited for different kinds of diffusion chromizing. The chromizing time required to obtain a certain zone thickness is shorter than with Armco iron used as a comparison and considerably shorter than with steels alloyed mainly with manganese or nickel. The powder pack method produces a 100 µm thick diffusion chromized zone at 1100°C in a 20% shorter time than with Armco iron. The good hardenability of the steel permits cooling to be carried out in air and still get strength properties suitable for machine construction purposes, as can be seen from tables 4 and 5. Table 6 shows that the austenising and water quenching plus tempering still improves the ductility of the steel.

These advantageous properties of the above described steels are due to the special alloying used and these properties exceed corresponding properties of previous steels. The low carbon content of the steels gives good toughness and allows fast diffusion chromizing, and the use of mainly ferrite stabilizing elements as alloying elements increases the growth rate of the chromized zone. The use of strong carbide formers prevents the formation of chromium carbides which would decrease the growth rate of the diffusion zone, and prevents grain growth during long chromizing heating.

WHAT WE CLAIM IS:-

65 1. Steel comprising from 0.01 wt% to 0.08 wt% carbon, from 0.1 wt% to 1.0 wt% 65

- silicon, from 0.5 wt% to 2.2 wt% manganese, from 2.0 wt% to 10.0 wt% chromium, from 0.01 wt% to 0.4 wt% molybdenum, from 0.001 wt% to 0.05 wt% aluminium (acid soluble) and at least one of the carbide forming elements, titanium, zirconium, niobium, and tantalum, so that the content of the carbide forming elements is more than 0.1 wt% and not more than 1.0 wt%, and wherein the balance of the steel is iron together with normal impurities.
2. Steel according to claim 1 containing from 0.01 wt% to 0.05 wt% carbon.
3. Steel according to claim 1 or 2 containing from 4.0 wt% to 8.0 wt% chromium.
4. Steel according to claim 1, 2 or 3 containing from 0.5 wt% to 1.0 wt% manganese.
5. Steel according to any of the preceding claims wherein the chromium acts as a ferrite stabilizing agent.
6. Steel according to any of the preceding claims, treated by annealing the steel at a temperature above 900°C in a chromizing agent until the chromium content of a chromized zone thereof exceeds 12 wt%.
7. Steel according to claim 6 wherein, after chromizing, the chromized steel has been quenched from a temperature from the range 900 to 1100°C.
8. Steel according to claim 7 wherein the steel has been quenched in water.
9. Products and articles made of the steel according to any of the preceding claims.
10. Steel according to claim 1 substantially as hereinbefore described.

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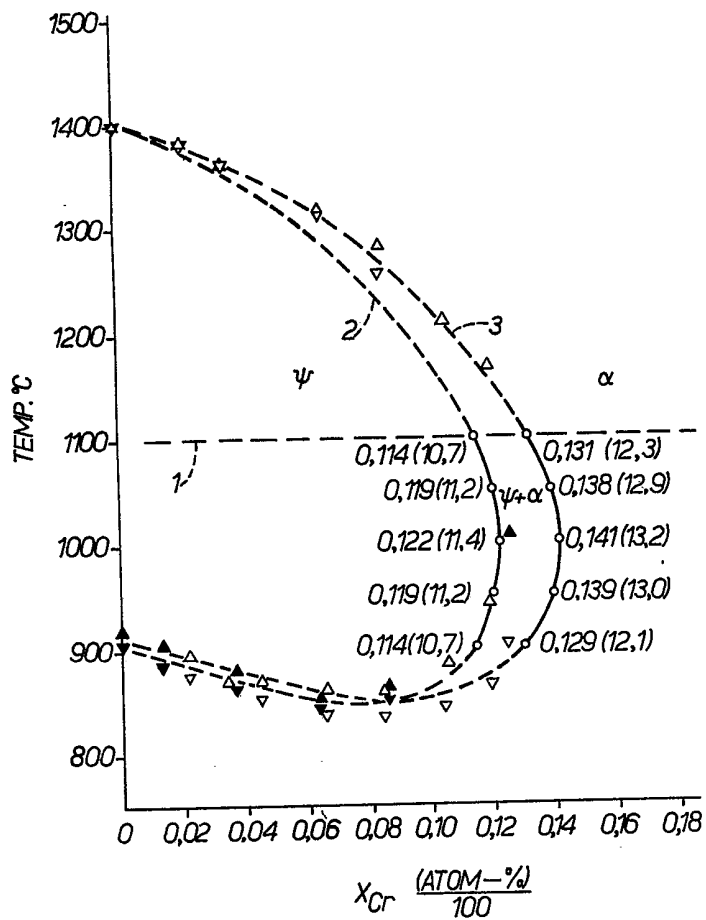
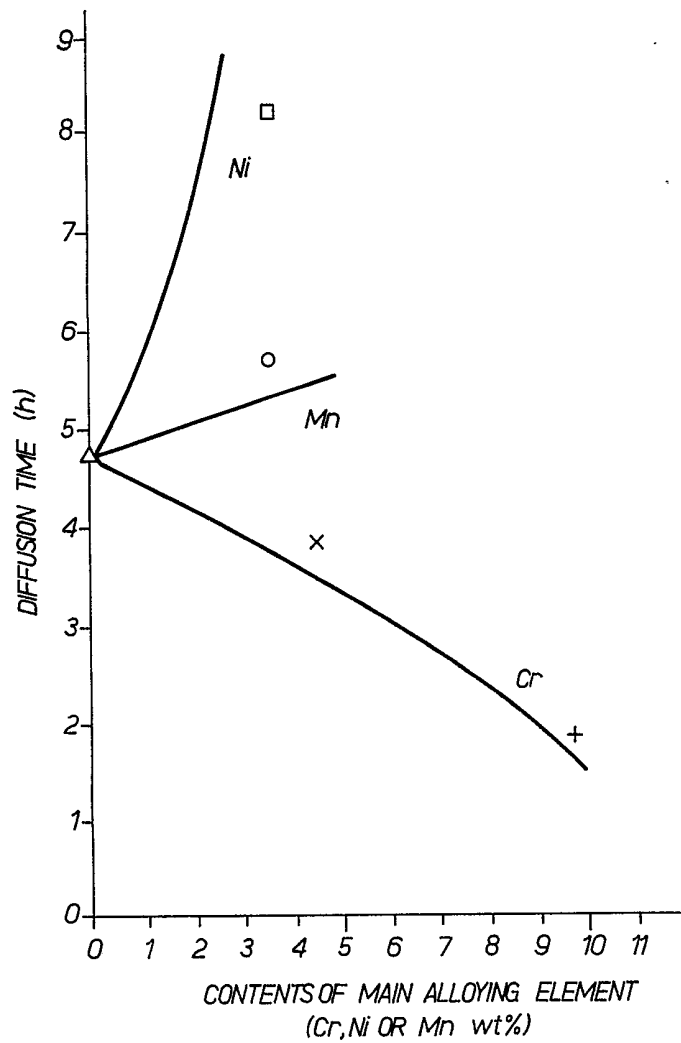
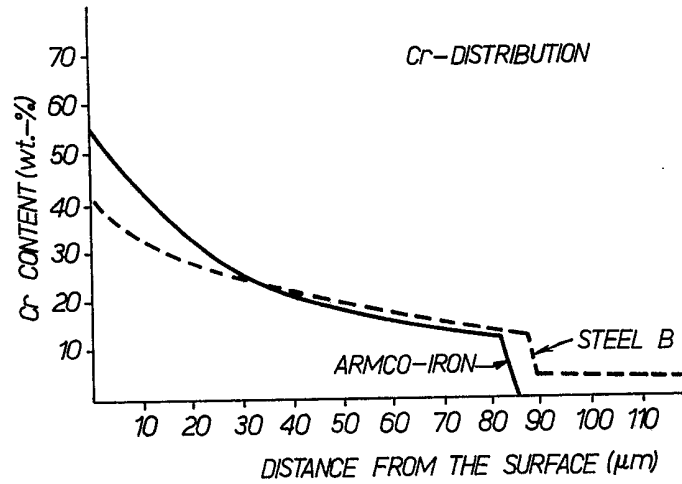


Fig.1.

**FIG.2.**

**FIG.3.**