No. 9

STAINLESS AND HEAT RESISTING STEELS

To produce order out of the apparent chaos of symbols and trade names used to denote the multifarious special steels which come within the category of stainless and heat resisting steels, the following paper endeavours to classify them with some semblance of reason and utility in view.

Such an attempt cannot fail to be incomplete since there are certain steels which elude classification.

Stainless and heat resisting steels have the common characteristic of containing chromium, and although they are considered in detail in two groups, each of which can be sub-divided into distinctive types, the line of demarcation cannot be drawn too finely, as all stainless steels have certain heat-resisting properties and *vice versa*.

Each sub-group has been further divided into distinctive types.

I.—Stainless Steels.

(A) **13 per cent. Chromium Steels.**—The resistance of straight chromium steels to corrosion was discovered by Brearley in 1913. Chromium induces passivity in the iron by forming a resistant film on the surface. The degree of passivity depends on the corroding agent and is in general proportional to the amount of chromium dissolved in the iron. The chromium exists partly as a carbide distributed throughout the material and partly in solution in the iron. It is the amount of the latter which determines the corrosion resisting properties.

The effect of increasing the chromium content of a steel is to increase its property of "air hardening." As in carbon steel, if the ferrite and carbide mixture known as pearlite is heated above its change point, it re-crystallises to gamma iron which can dissolve the carbide to form austenite. On air cooling the chromium steel, however, hard brittle martensite is produced, an effect analagous to that obtained by quenching carbon steel. The normal pearlitic state can only be obtained by slow cooling in the furnace. The martensite obtained by this air cooling may be tempered to give the desired physical properties.

The effect of the carbon content is very much accentuated in this type of steel. Thus, a 13 per cent. chromium steel with carbon content of 0·3 per cent. is approximately equivalent, so far as hardening and tempering is concerned, to an ordinary steel containing 0·9 per cent. of carbon.

Very mild varieties are known as " Stainless Iron " and can be rolled into turbine blading section, etc.

The intermediate types are now in general use for all classes of engineering work.

The high (0·3 to 0·4 per cent.) carbon material is used for cutlery, generally in the martensitic state as this is the best condition for resisting corrosion. It is given a slight temper to take out the extreme brittleness.

(B) **18 per cent. Chromium (+ 2 per cent. Nickel) Steels.**—As the chromium content is increased above 13 per cent., the resistance of the steel to certain kinds of corrosion increases. Thus, a steel with 17 to 18 per cent. of chromium resists contact corrosion especially with non-ferrous materials, which is not the case with 13 per cent. chromium steels.

At the same time, however, the change points tend to disappear and with them the property of air hardening. The increased chromium content gives rise to increased grain size with the result that the steel can only be hardened by further modification of the composition, *i.e.*, either by increasing the carbon content or preferably by introducing 2 per cent. of nickel.

Thus we find in this sub-group, stainless steels containing 18 per cent. chromium and 2 per cent. nickel where hardening properties are required and stainless irons containing 18 per cent. chromium only for purposes where no hardening is necessary.

In both cases the carbon content is adjusted to give the requisite physical properties.

(C) **18 per cent. Chromium, 8 per cent. Nickel Steels.**—If the nickel content of type (B) be increased to 8 per cent., the hardening properties disappear, the increased nickel stabilizing the austenite condition instead of the iron remaining as ferrite as in straight 18 per cent. chromium steels. The steels in this group are known as the 18/8 series and were first patented by Messrs. Krupp. Some manufacturers prefer to use a 16 per cent. chromium and 10 per cent. nickel steel which is said to give more constant hardness over a range of temperatures. A further type containing 12 per cent. chromium and 12 per cent. nickel is used for articles produced by " deep drawing " processes. The homogeneity of this material under all conditions would appear to make it ideally suitable as a corrosion resisting steel. Further, its freedom from air hardening effects and the retention of great ductility and toughness when coarsely grained, should make it ideal for welding. Actually it has two disadvantages. Firstly, the elastic limit is low. Secondly, if it is either cooled slowly from about 1,000° C. or reheated between 500° and 900° C., the chromium carbide particles previously referred to are thrown out of solution and migrate to the grain boundaries. If the steel is now exposed to corrosive action, it is attacked in the carbide denuded areas adjacent to the grain boundaries in such a manner as frequently to cause the entire mass of the steel to disintegrate. The worst effects are obtained by reheating between 600° and 700° C. This causes serious trouble in welding operations, where there must of necessity be a band more or less wide, which during the operation has reached this critical range of temperature. Failure from this cause is known as " weld decay."

The evil effects so produced can be cured by correct heat treatment which consists of quenching from 1,000° C. Unfortunately this treatment is not always practicable in the case of large fabricated jobs.

(D) **18 per cent. Chromium, 8 per cent. Nickel Steels with additions.**—This fourth group consists of the austenitic steels referred to in group (C) with modifications to overcome their inherent weaknesses.

The first step in producing a steel free from weld decay was to reduce the carbon content to a minimum. This was difficult owing to the affinity of chromium for carbon, but was made possible by the introduction of the high frequency electric furnace. The attempt was partially successful, but a carbon content of as little as 0·03 per cent. would be necessary entirely to eliminate the trouble.

Secondly, it was found that if the material was held at a temperature of 900° to 920° C. for about 36 hours, the carbides which had migrated to the grain boundaries during the heating up process, tended to coagulate into globules and distribute themselves throughout the mass of the material. The material was now proof against the ill effects mentioned without further heat treatment. This process is, of course, expensive and cumbersome.

Thirdly, other elements were added to stabilize the carbide in solution. Various manufacturers claim that steels containing respectively 0·1 to 2·0 per cent. titanium, 0·3 to 2·0 per cent. vanadium and 0·3 to 1·5 per cent. tungsten are free from intergranular attack. Titanium is the usual element added and since its beneficial action is caused by the formation of another carbide, the amount required is proportional to the carbon content. A low carbon content is advantageous since the bright appearance and polish obtained vary inversely with the titanium content.

The addition of vanadium has the same effect as titanium but it is more expensive.

Tungsten and silicon both succeed in partly but not completely checking the susceptibility to attack.

Increasing the chromium content also has a beneficial effect as the degree of impoverishment of near-boundary areas by the migration of chromium-rich carbides to the boundaries is reduced. Steels of this type are largely used in heat resisting work.

Up to 4 per cent. of molybdenum is frequently added as it gives extra resistance to certain types of corrosion and improved shock resisting qualities.

Both molybdenum and titanium also add a little to the elastic limit and maximum strength of the material.

The materials in groups (C) and (D) can be obtained in a higher tensile condition by cold work. The elastic limit by this means can be increased from 20 to 50–60 tons per sq. in. and the maximum strength from 45 to 60–70 tons per sq. in. The steels can be softened again by heating to 1,100° C. followed by rapid cooling.

II.—Heat Resisting Steels.

The requirements of a steel for use at high temperatures are threefold.

In the first place it must be able to be exposed to the action of both the high temperature and the agent producing it without any appreciable loss of its substance.

Secondly, it must be able to do this with only such reduction of strength as leaves it still suitable for its purpose.

Thirdly, it must not become brittle under prolonged exposure to heat.

As a steel is heated in air it forms a scale of iron oxide. This is first visible as a colour going through the " temper colour " range from pale straw to grey. Above the temperature necessary for the latter condition, oxidation takes place rapidly and quickly forms a skin. The type of this skin determines the heat resistance of the steel. Porous, loose skins will quickly grow and fall away. Non-porous adherent skins help to prevent further oxidation. As the temperature is raised, all skins eventually become porous and the steel enters on its " free scaling " range. Mild steel begins to scale appreciably after about 500° C.

So far as the agent applying the heat is concerned, experiment shows that atmospheres containing considerable quantities of water vapour and either CO_2 or SO_2 cause a much greater amount of oxidation than air at a similar temperature.

Turning to strength at high temperatures, the first consideration is that at temperatures as low as 400° C., ordinary carbon and many alloy steels yield plastically and eventually break under loads producing stresses considerably less than the figures for the maximum strength obtained from ordinary tensile tests at the same temperature. This flow under continued stress is known as " creep." At ordinary temperatures this creep takes place initially, but the distorted crystals have a " strain hardening " effect and creep ceases. At higher temperatures however, re-crystallization takes place rapidly and removes the induced hardness, thus allowing creep to continue. The design of parts for use at a particular temperature is made on the basis of the maximum stress which the material will stand at that temperature without creeping at a greater rate than can be permitted in the parts in question.

The effect of high temperature on toughness is also important. Ordinary carbon steels become brittle between 300° and 500° C.

Many alloy steels of the nickel-chrome-molybdenum-vanadium type become brittle after prolonged exposure to temperatures of 400° to 450° C.

A heat resisting steel should therefore have a high free scaling temperature, a high resistance to creep and be free from embrittlement at the temperatures at which it is required to be used.

The following shows the effect of adding various elements on the heat resisting properties of ordinary steel.

Chromium added to carbon steel increases its free scaling temperature proportionally to the chromium content. Scaling commences in 13 per cent. chromium steels at 850° C., in 18 per cent. at 1,000° C., and in 30 per cent. above 1,100° C.

Again, 13 per cent. chromium steels are stronger than mild steels, but this strength falls off quickly above 600° C. Raising the chromium content to 18 per cent. lowers the strength between 450° and 600° C.

Experiment suggests that 13 per cent. chromium steels do not possess any appreciable embrittlement range, but in the higher straight chromium steels the grain growth above 700° C. is considerable and they are of little use for any service in which shock resisting qualities are required.

Nickel seems to have little effect on scaling up to about 20 per cent. when increased protection is given to a chromium steel from oxidation by air, oxygen, steam or CO_2. Against sulphurous gases, however, the protection is actually decreased.

As regards strength, the austenitic chromium-nickel steels of the 18/8 type are distinctly stronger than the 13 per cent. chromium steels above 450° C. Increasing the nickel content beyond 8 per cent. appears to counteract embrittlement and above 20 per cent. definitely increases the limiting creep stress. From 500° C. to 900° C., however, the austenitic steels are likely to suffer from intergranular weakness in the presence of corroding agents.

The addition of silicon increases very markedly the resistance to oxidation. It also increases slightly the strength at high temperatures. Further, it raises the change points of chromium steel and thus reduces the danger of cracking by hardening which exists with steels with change points below the free scaling temperature. Finally, it helps to overcome inter-crystalline weakness in austenitic steels. Against this, its use is limited by the fact that above 2 to 3 per cent. it causes general embrittlement.

Tungsten has little effect on the oxidation resisting properties, but it adds considerably to the strength at high temperatures.

Molybdenum is now being used in certain of the 8 per cent. and 13 per cent. chromium steels with the object of increasing the creep strength at high temperatures.

The following is a list of the various types of heat resisting steels in common use.

1. Straight Chromium Steels with the Addition of Silicon.

(A) 8 *per cent. chromium,* 3 *per cent. silicon.*

This steel is widely used for internal combustion engine valves.

The 3 per cent. of silicon added to the chromium is sufficient to give protection from scaling up to 850° C. It also raises the change points sufficiently to stop any tendency for the steel to harden on cooling from its working temperature. This steel can be easily forged and stamped.

(B) 13 *per cent. chromium steels.*

With the addition of a small amount of silicon (0·5 to 1·5 per cent.) this steel is used for I.C.E. valves. It scales at a slightly lower temperature than (A) and has not quite the same strength at high temperature.

(C) 20–30 *per cent. chromium steels containing* 2–3 *per cent. silicon.*

These steels have a very high free scaling temperature. They do not respond to heat treatment but are very subject to grain growth and consequent embrittlement at high temperatures. They cannot therefore be used under severe conditions of stress. Certain steels have a small quantity (2 to 3 per cent.) of nickel added to retard the grain growth to some extent.

2. Austenitic Steels.

(*a*) *The* 18/8 *type with additions.*

(i) The ordinary 18/8 steel is used as a heat resisting steel with small additions of titanium and tungsten or silicon, for services where resistance to intercrystalline attack is needed up to a red heat.

(ii) For higher temperatures, 1 to 2 per cent. silicon and up to 4 per cent. tungsten is added which gives a steel with considerable scale resisting properties and very good all-round strength at high temperatures.

(iii) From the 12/12 type a steel used as a super-quality valve steel and for heat resisting drop stampings generally is derived, by the addition of 1 to 2 per cent. silicon and 2 to 3 per cent. tungsten.

(*b*) *Steels containing* 20–25 *per cent. chromium,* 10–12 *per cent. nickel with the addition of silicon and usually tungsten.*

The free scaling temperature of steels of class (*a*) can be increased by raising the chromium content from 18 to 20–25 per cent. while the raising of the nickel content slightly gives better shock resisting properties. 1 to 2 per cent. of silicon is always added, with about 3 per cent. tungsten if extra strength at high temperature is required.

Steels of this type are widely used in all classes of heat resisting work.

TABLE 1.

List of the More Important Stainless and Heat Resisting Steels Produced by Firms in the Sheffield District.

Type of Steel.	Messrs. English Steel Corporation.		Messrs. Firth-Brown.		Messrs. Firth-Vickers.		Messrs. Hadfield.		Messrs. Jessop.		Messrs. S. Fox.		Messrs. Brown-Bayley.	
	Name.	Remarks.	Name.	Remarks.	Name.	Remarks.	Name.	Remarks.	Name.	Remarks.	Name.	Remarks.	Name.	Remarks.
Stainless steels—														
(A) 13% chromium ..	Immaculate 1 Immaculate 2	Stainless iron	FI FG FH	Stainless iron	FI FG FH		Galahad A Galahad B Galahad C Galahad D	Stainless iron	R1 R2	Stainless iron	Silver Fox 10 Silver Fox 11 Silver Fox 12 Silver Fox 13 Silver Fox 14	Stainless iron	Brearley Inventor Engineer-ing Cutlery	Stainless iron
(B) 18% chromium, 2% nickel	Immaculate 7		Saitie		S 80		Galahad E		R4		Silver Fox 17	18% Cr Stainless iron (no nickel)	Brearley K Two score	18% Cr Stainless iron (no nickel)
(C) 18% chromium, 8% nickel and modifications	Immaculate 4 Immaculate 3 Immaculate SS	18/8 16/10 12/12	Staybrite DDQ	12/12	Staybrite DDQ		Era CRI Era CRDD	18/8 12/12			Silver Fox 18 Silver Fox 20 Silver Fox 21	18/8 12/12	Anka 18/8 Anka 15/11 Anka 12/12	
(D) 18% chromium, 8% nickel with additions	Immaculate 3W Immaculate 3P Immaculate 3M Immaculate 3K		Staybrite FST Staybrite FDP Staybrite FMB Staybrite FML	18/8 ·6 W 18/8 ·7 W ·8 Ti 18/8 3 Mo 18/8 1·5 Mo low carbon	Staybrite FST Staybrite FDP Staybrite FMB Staybrite FML		Era CR IS Era CR 2 Era CR 4S	18/8, ·6 Ti 18/7, 3·5 W 2·0 Cu 18/9, 2·5 Mo	B4 Any	16/10, ·5 Ti 2·5 Mo	Silver Fox 22 Silver Fox 24	18/8 + Ti 18/8 + Ti + 3 Mo	Weldanka Weldanka B B.B. 4K	21/9, 2 Si, ·25 Ti 13/11, 2 Si, ·5 Ti 17/10, 3 Mo
Heat resisting steels—														
Chrome-silicon—														
(A) 8% chromium, 3% silicon	Si CR		S.L.V.		S.L.V.		Hecla NS		H3	6 Cr, 1·5 Si	Red Fox 21 Valmax	8 Cr, 3 Si ·75 Mo	Q.S. Q.S.S.	8 Cr, ·7 Si 8 Cr, 3 Si
(B) 13% chromium, ·5–1·5% silicon			F.A.S.		F.A.S.						Red Fox 10		Pyralloy	
(C) 20–30% chromium, 1–2% silicon	Pyrista	26–29 Cr 2 Ni, 2 Si, high carbon	Vesuvius	30% Cr 1–2 Si high or low carbon	Vesuvius Pyrista		Era HR 4	29 Cr, 1 Si			Red Fox 11 Red Fox 12	20-22 Cr, ·6 Si 28-30 Cr, 1·5 Si, 2·5 Mn	Lowscore Kalloy	22 Cr 27 Cr
Austenitic—														
(*a*) 18% Cr, 8% Ni, with additions—														
(i) Low heat 18/8 resistance			Staybrite F.D.P.		Staybrite F.D.P.								Weldanka Weldanka B	
(ii) High heat 18/8 resistance	Immaculate 4w	20/7, 1·5 Si, 4 W			Immaculate 4 W		Era HR2 Era HR1	20/7, 1·5 Si 21/7, 1·5 Si, 4W					Hotspur D	22/6, 1 Si ·3 W
(iii) High heat 12/12 resistance	Immaculate 9	13/12, 1·5 Si 3 W			F.V.S.				G2	12/12, 1·5-2 Si, 2 W			Hotspur A	12/12, 1 Si, 2W
(*b*) 20-25% chromium, 10-12% nickel, with additions			HR 2610 HR Crown Max	26/10, 2 Si 24/12, 1·5 Si, 3 W	Immaculate 9 HR 2610 HR Crown Max									
(*c*) 25% chromium, 20% nickel with additions	Immaculate 5	25/20, 2·5 Si	HRMC 2520	25/20, 2 Si	Immaculate 5						Red Fox 31	25/20, 2 S	Hotspur C Hotspur E	25/20, 1·5 Si 25/20, 1·5 Si, 2·5 W
(*d*) 15% chromium, 25% nickel with additions	Immaculate 6	15/25, 2 Si, 4 W			Immaculate 6		Era ATV	14/28, 1·5 Si, 4 W					Hotspur B	15/25, 2·5 Si
(*e*) 10-12% chromium, 35% nickel, with additions	Macloy	11/35 1·5 Mn					Hecla ATV	11/35, 1·5 Mn						
(*f*) 15% chromium, 65% nickel	Vikro	15/65			Vikro									

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TABLE 2.

MATERIALS ACCEPTED FOR ADMIRALTY WORK.

Material.	Typical compositions.							Uses.	Remarks.
	C	Cr	Ni	Si	Mn	S	P		
Stainless iron	0·12	12·5 to 13·5	0·5	0·25	0·3	0·03	0·03	Reaction turbine blading	—
13 per cent. Cr	C	Cr	Ni	Si	Mn				
Firth-Vickers "F.G." ..	0·15 to 0·35	12 min.	1 max.	0·5 max.	—			Seats and spindles for valves subject to superheated steam; sometimes used for I.C.E. valves	—
Brown-Bayley's "Cutlery," etc.	0·3	12	—	0·5	0·5				
18 per cent. Cr, 2 per cent. Ni	C	Cr	Ni	Si	Mn				
Firth-Vickers "Saitie"	0·25 max.	16 to 20	1 min.	0·5 max.	1 max.			Valve spindles	Superior to 13 per cent. Cr varieties, particularly for resistance to contact corrosion with graphite packings.
Brown-Bayley's "Two Score"	0·15 to 0·25	16 to 20	1 min.	0·5 max.	0·91				
Hadfield's "Galahad E" ..	0·18	17	2	0·3	0·3				
18 per cent. Cr, 8 per cent. Ni	C	Cr	Ni	Si	Mn	Ti	Al		
"Weldanka"	0·2	18	7	1–3	1	—	—	Impulse turbine blading..	—
"Stalyblade"	0·22	20·24	8·56	1·2	0·31	1·35	—		
"Stayblade Max"	0·11	18·7	8·46	0·72	0·35	0·86	1·52		
8 per cent. Cr, 3 per cent. Si	C	Cr	Si	Mn	Va	S	P		
Hadfield's "Hecla N.S."	0·4 to 0·5	8 to 9	3 to 3·5	0·3 to 0·5	0·2 to 0·3	0·03 max.		Valves for I.C.E.	—
Jessop "H.3," etc. ..	0·55 to 0·65	6 to 7	1·5	—	—	—	—		
High Nickel Steels.	C	Cr	Ni	Si	Mn				
Hadfield's "Hecla A.T.V." ..	0·36	11	36	0·1	1·2			Impulse turbine blading subject to superheated steam	—
Heat Resisting Steels.	C	Cr	Ni	Si	Mn	W			
Hadfield's "ERA, HR.1" ..	0·35	21	7	1·4	0·5	3·75		Parts subject to furnace gases: superheater supports, combustion tubes, etc.	—
Firths "H.R. Crown Max" ..	0·3	22·96	11·78	1·81	0·36	3			
"Immaculate 4W"	0·335	19·68	7·36	1·34	0·48	4·13			

(*c*) *Steels containing* 25 *per cent. chromium,* 20 *per cent. nickel, with silicon and possibly tungsten.*

If the nickel content in (*b*) is increased to 20 per cent., the free scaling temperature is again raised and the strength increased in steels of otherwise similar compositions. 1 to 2 per cent. of silicon is included and occasionally about 2 per cent. tungsten.

Steels of this type are finding increasing favour for general heat resisting work.

(*d*) *Steels containing* 15 *per cent. chromium,* 25 *per cent. nickel, with silicon and tungsten.*

These steels, usually containing 4 per cent. tungsten in addition to 1 to 2 per cent. silicon, were formerly employed for valves in high power petrol engines and many other heat resisting services. They have very considerable strength at high temperatures, but are difficult to forge and are giving way in many instances to steels of types (*a*), (*b*) and (*c*).

(*e*) *Steels containing* 10 *to* 12 *per cent. chromium and* 35 *per cent. nickel with additions.*

This type of steel containing about 1·5 per cent. manganese does not perhaps come strictly under the heading of heat resisting steels. It possesses very good resistance to corrosion and erosion with considerable strength up to 400/500° C. It is largely used for turbine blading.

(*f*) *Materials containing* 15 *per cent. chromium with a very high nickel content* (60 *to* 70 *per cent.*).

This material is more nearly a nickel-chrome alloy than a steel, but is included here to complete the list and also as it was the original heat resisting material. It possesses very good resistance to oxidation combined with great strength at high temperatures. Against this it is very difficult to forge and the cost is very high. Moreover, in sulphurous atmospheres its scale resisting properties are considerably reduced.

Attached for reference purposes are tabular statements :—

(1) Giving various trade alloys allocated to the grades indicated above (Table 1).

(2) Showing the particulars of some materials accepted for Admiralty work (Table 2).