The Structure and Properties of Precipitation Hardened Stainless Steels[*].

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〈**Abstract**〉

There is a requirement for readily formable corrosion resistence alloys of higher strength. The alloy must also be weldable. such alloys are the martensitic precipitation hardening steels such as the American PH series e.g. 17—7 PH. British practice uses the term "Controlled Transformation Steel" e.g. FV 520 (s) indicating the use of composition and heat treatment to control the austenite to martensite transformation.

The composition, microstructure, properties and applications of these steels together with full production sequence will be discussed.

析出 硬化鋼의 組織과 性質

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〈요 약〉

고장력강으로서 가공성 및 내식성 그리고 용접성이 좋은 철강재료가 바로 마르텐싸이트系 석출경화형 합금강이다.

이를 미국에서는 PH系 합금강(例 17—7PH)이라 부르며, 또한 영국에서는 변태조절강(Controlled Transformation steel)이라 부른다.

이들의 성분조성 및 全 생산열처리 공정과 이들의 성질 및 응용에 대하여 간단히 논하려 한다.

The engineering value of metals, as a whole, is associated with their good strength coupled to high ductility. If you add the ability to withstand corrosion and the ability to be easily formed to shape you will have an ideal engineering material.

Allotropic phase transformations are not uncommon in metals, indeed are important in titanium and uranium alloys but the transformation in iron have special significance.

The body centred cubic structure of ferrite or martensite gives a high yieldstress but low work hardening ability, i.e. a low ratio of tensile strength to yield stress. In this condition the metal can safely be used in service to a high percentage of its tensile strength. However the low work hardening rate makes large deformation, particularly in sheet material,

difficult.

On the other hand the face-centred cubic austenitic phase, is associated with a low yield stress but high work hardening. In this condition the metal has excellent formability.

The effect of adding chromium and nickel to iron to stabilize the austenitic phase to room temperature has been used for over fifty years and is the basis of the AISI 300 series of alloys based on 18% Cr, 8% Ni. The chromium mainly imparting the excellent corrosion resistance.

The yield stress of the AISI 300 series range from 30—40Ksi with tensile strengths 80—90 Ksi. Cold work can be used to increase the strength but ductility decreases considerably and the effect is completely lost with welding.

By careful control of the composition and heat treatment it is possible to obtain a steel which can be formed in the austenitic condition but by using a fairly low temperature heat treatment, transformed to the high yield stress martensitic condition. Such steels have been available for a number of years and are known as the controlled transformation steels.

The controlled transformation steels were developed along side similar alloys which were fully martensitic on cooling from annealing temperatures. Both types of steel rely on precipitation hardening within martensite to increase their strength levels.

The American PH type steels include both types i.e. "Controlled Transformation Steels" and "Fully Transformable maraging stainless steels'

The temperature for the onset of the martensite transformation (Ms temperature) in pure iron is about 540°C but is significantly reduced by alloying addition.

Carbon has by far the most pronounced effect reducing Ms by 420° for 1%C addition. The Mf temperature is similarly reduced from 400°C
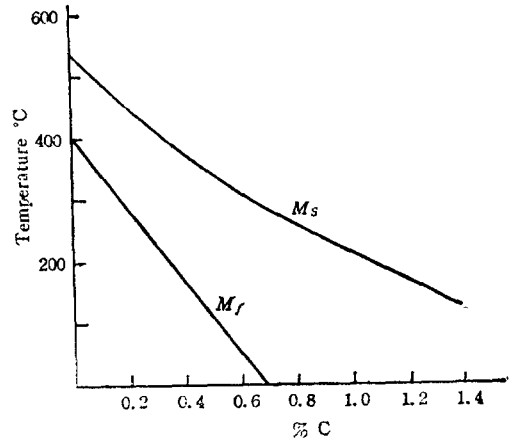

Fig 1

The temperature range Ms-Mf does not alter very much and is about 140°C.

The minimum chromium content for acceptable corrosion resistance is 12% and with this base i.e. Fe—12%Cr the Ms temperature is about 300°C

The effect of other elements are shown below.

Element	Depression of Ms for 1% element
C	470°C
Al	55°C
Mn	33°C
Cu	32°C
Mo	21°C
Cr	17°C
Ni	17°C

With large alloying additions the austenitic martensite transformation is lowered down so much that metastable austenite is produced on cooling to room temperature, as occurs in the 18/8 steels.

The microstructure of Cr/Ni steels cooled quickly from the austenite region can be represented on a modified Schaeffler diagram in terms of chromium and nickel equivalent compositions.
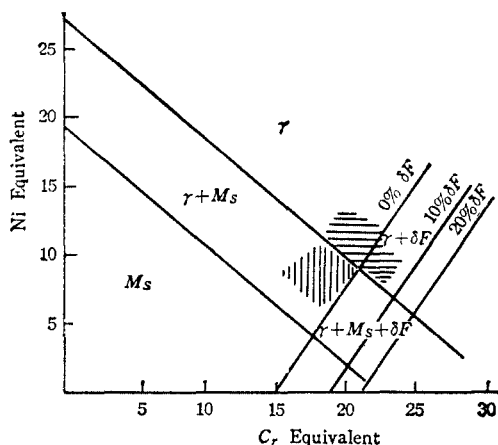
Fig 2

Apart from austenite and martensite the other important phase is the body centred cubic δ-ferrite phase.

The chromium effective elements are all δ-ferrite stabilising elements, the nickel elements all stabilise austenite.

The Controlled Transformation Steels lie close to the Austenite/Austenite + Martensite boundary. But there are other constraints on their composition. Corrosion resistance has already been mentioned.

The carbon content should be kept low because of the tendency to form carbides and reduce ductility particularly with welding.

δ-ferrite causes a marked loss in strength to the alloy as well as lowering the toughness. It occurs as stringers in the rolled product and cannot be modified. Transverse toughness is particularly effected.

However small amounts of δ-ferrite improve hot ductility and reduce the tendency for hot cracking during welding.

Thus the compositional range of C.T.S. steels is severely restricted and is shown on the modified Schaeffler diagram.

The fully transformable maraging stainless steels have lower nickel and chromium equivalents.

The composition of two C.T.S. steels is as follows.

	C	Si	Mn	Cr	Ni	Mo	Cu	Al
American PH17—7	0.07	0.3	0.6	17	7	—	—	1
British FV520(S)	0.08	0.5	1.7	16	6	1.8	2	—

	Ni	Cr
Their Ni and Cr equivalents are PH 17—7	9.4	23.1
FV520(S)	9.8	19.6

The alloy are only just sufficiently stabilised to produce austenite on cooling from their annealing temperature. As a consequence subsequent heat treatment tenders the alloy martensitic.

Cooling the alloys to about −80°C transforms most of the austenite to martensite. −80°C is about the lowest heat treatment temperature which is industrially viable for large engineering components.

We said earlier that the Ms-Mf range was about 140°C and thus cooling from 20°C to −80° C can not cover the full transformation range. It is common to have about 5% martensite on initial cooling from annealing but even so residual austenite is usually present after cooling to −80°C

The amount of residual austenite increases if the metal is held at room temperature for lengthy periods after annealing. The austenite becomes stabilised by the diffusion of carbon and nitrogen.

The alternative method of controlling the transformation to martensite depends on the precipition of carides. The alloy is tempered at 750°C which precipitates chromium carbide from solution. This is called conditioning. Once again we find that with the amount of carbon in these alloys the Ms temperature can only be raised by about 100°C by this treatment.

A third methed of obtaining martensite is possible. Cold deformation above the Ms temperature results in transformation to martensite but this method is of limited use for general

engineering and is mainly used to obtain high strength stainless steel wires.

The strength of the martensite formed on transformation is not high because of the low carbon content and in order to obtain the strength levels required additional strength is obtained by precipitation hardening. A variety of elements have been used. Titanium and aluminium give intermetallic phase while copper is precipitated in its elemental form. If the martensite has been produced by refrigeration, or by a cold work, chromium and molybdenum carbides are also precipitated.

Although the heat treatment of these alloys may appear complex it has the advantage that after forming and fabricating in the austenitic condition further heat treatment is limited to a maximum of 750°C for conditioning. Thus distortions associated with high temperature heat treatments(900—1100°C) are not encountered and oxidation are not severe.

The full production sequence for these steels is as follows:

Melting and casting is the same as other stainless steels with vacuum treatment preferred to give a cleaned steel with low gas content.

Initial working is again as for other stainless steels.

The austenitising temperature must be sufficiently high to dissolve the carbides as otherwise the alloy would transform on cooling.

On the other hand grain growth should be limited so once again with these steels a fine balance has to be obtained. A further factor to be considered is the δ-ferrite phase. a high annealing temperature forms δ-ferrite which will be stable on cooling. Control of the annealing temperature is therefore of prime importance. 1040—1060°C is widely recommened although temperature as low as 930°C are used with some of these steels. 30 minutes is usually sufficient for this treatment.
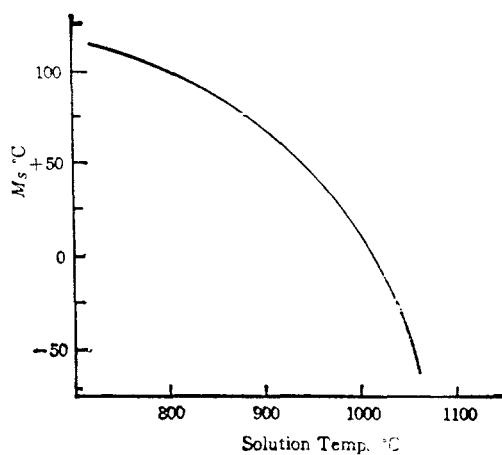
The effect of the annealing temperature on

Fig 3

the martensite transformation temperature is shown on the diagram. As these materials are must widely available as sheet materials a sufficiently high cooling rate can be achieved by simple air cooling. When forging material is used oil quenching is usually necessary. In any case it is important to prevent carbide precipitation during the cool from the annealing temperature as this would raise the Ms temperature above room temperature.

The microstructure at this stage consists of austenite grains with some ferrite elongated in the rolling direction.

The material is formed and fabricated in this condition and the material is usually delivered by the manufacturer in the solution annealed condition.

As mentioned before there are two main methods of inducing the transformation to martensite; refrigeration or carbide precipitation.

Refrigeration is carried out at −75 to−30°C. Although the martensitic transformation is mainly athermal i.e., does not depend on time, with highly alloyed steels the reaction is very sluggish and periods of up to 8 hours are required to ensure maximum transformation of

the austenite. Even so significant amounts of retained austenite will remain particularly when there has been a long delay after the solution anneal treament. No carbides are present at this stage.

The second heat treatment method is to heat the austenitic material to about 750°C for between 1 and 4 hours and then air cool.

The mainly chromium carbide, $M_{23}C_6$, is precipitated out of solution. The carbide usually occurs as small particles at the austenite grain boundaries but some intercrystalline precipitation also occurs. On heating to 750°C any martensite which had formed at room temperature will revert to austenite during this second heat treatment and there is evidence from electron-microscope studies that dislocation tangles are formed in the austenite associated with the defect structure of the martensite. These dislocations act as nucleating sites for the carbides. In these regions the carbide distribution appears to be along the boundaries of the initial martensite plates.

An alternative possibility is that nucleation of the precipitates occurs in the martensite phase during the heating up period to the 750°C.

This fine distribution of intergranular carbides produces a higher strength final product and is also less liable to corrosive attack.

By combining the refrigeration process with the 750°C treatment it is possible to ensure that almost all the carbide is precipitated as fine $M_{23}C_6$ and the material is almost fully martensite on cooling to room temperature.

The strength of the martensite at this stage in the heat treatment is about 750N/mm² and, as indicated earlier, the final strength of the alloys is obtained by a final tempering or aging treatment. This is carried out in the range 450 —550°C, the higher temperature being used for tougher alloys.

In the case of the refrigerated alloys there is a supersaturation in carbon as well as the

secondary hardening elements. This results in the higher temperature phase $M_{23}C_6$ above about 500°C. In those steels containing molybdenum $M_2(CN)$ is formed which enhances high temperature properties by increasing the resistance to softening.

The main precipitation hardening reaction is due to the elements Al, Ti and Cu which are soluble in the austenite but become supersaturated in the transformed martensite.

Al and Ti form the intermetallic phase with Ni whilst Cu is precipitated in its elemental form as small rods. The precipitaion reaction is sluggish and seldom achieves maximum hardness when aged below 500°C.

0.2% proof stress of between 1000 and 1500 N/mm²(180,000—220,000Psi) can be obtained as the result of this aging treatment.

The complete heat treatment cycle is indicated in fig.4 but it would nomally include a break in time for the forming and fabrication stage.

<Fig 4>
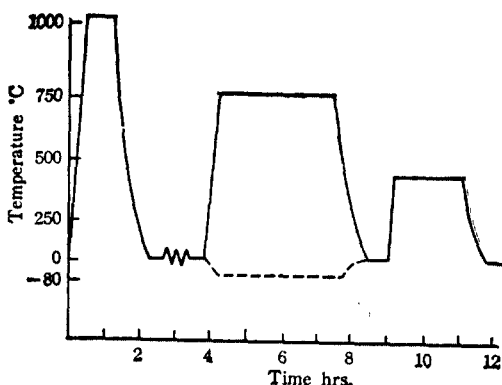
The main properties of this class of steel have been mentioned earlier. These are briefly high yield stress and corrosion resistane.

The particular values of the properties depend very much on the composition and processing route. The conditioning treatment at 750°C reduces capacity for age hardening so results in

strength levels at the botton end of the range (180,000 Psi).

However the low carbon martensite formed by this treatment causes less distortion than that produced by refrigeration.

Aging after refrigeration gives proof stress between 1200 and 1500N/mm²(200,000—220,000 Psi). In both these conditions the ductility will be between 8 and 12%, greater ductility can be obtained by aging at up to 550°C with a corresponding loss in strength.

To obtain the highest strength levels with these steels 40% cold work is used to induce the martensite transformation but by this method the ductility will only be 2—3% even though strengths of 220,000—250,000 Psi. are possible.

Since these materials are low C martensitic they all show low work hardening rates and they have yield/tensile strength ratios of 0.8 —0.9.

Being body centred cubic their high temperature strengths are only moderate but have excellent high temperature strengths up to 500°C particularly for short periods as encountered in many aerospace applications.

The fatigue resistance of the alloys is good and can be improved by nitriding. Their corrosion resistance is similar to that of the 18/8 type austenitic steels(The AISI 300 series). The Mo bearing steels improves the resistance of acid attack in the same way as in their austenitic counterparts. Equally, however, these alloys are susceptible to stress corrosion and corrosion fatigue.

The weldability of these alloys is one of their most important properties, mainly due to their low carbon content. Tungsten Inert Gas (TIG) welding is the usual method used although any method suitable for austenitic steels may be used. Small quantities of δ-ferrite are beneficial in welding, giving the alloy resistance to hot cracking of the weld metal. Neither pre-heating of the component nor interpass heating is needed.

To reduce the distortions associated with phase changes it is common practice to weld after the component has been transformed to martensite. The heat affected zone can then be transformed by refrigeration and the whole structure age hardened to the desired strength levels.

The weld matal is usually lower in Nickel being one of the direct hardening maraging stainless steels. The weld metal then transforms directly to martensite on cooling.

The aluminium bearing grades are rather more difficult to weld than the copper and titanium alloys because of the risk of oxidation of the aluminium producing plates of alumina and a brittle weld. The alloy can also be brazed.

As well as their mechanical and chemical properties economic aspects determine the applications that are suitable for these alloys.

Firstly the materials are highly alloyed steels basically similar to the 300 AISI series. Their somewhat lower nickel content gives them an initial cost advantage but this is more than offset by the close limits which are imposed on the composition. Most manufacturers produce the fully hardenable steel as well so that the two steels together have a wider composition range. This is more acceptible for the producer. Close control of the early working stages is also necessary. If they are over heated too much δ-ferrite will be produced.

These steels are therefore difficult to produce with uniform properties and this is reflected in their costs.

However their properties make them valuable materials for engineering. They are used for aircraft structures and skin materials.

It is also used for light weight honeycombe structures, in this case the sheets are usually brazed.

There are many military applications both for missiles and aircraft and for light weight ground equipment.

In many applications the direct hardening steels are used for forged components welded to the controlled transformation sheet alloys.

The controlled transformation steels show the sophisticated control steels, taking advantage of the properties of the different structures obtainable in steels. The range of applications for these materials will increase in the coming years.