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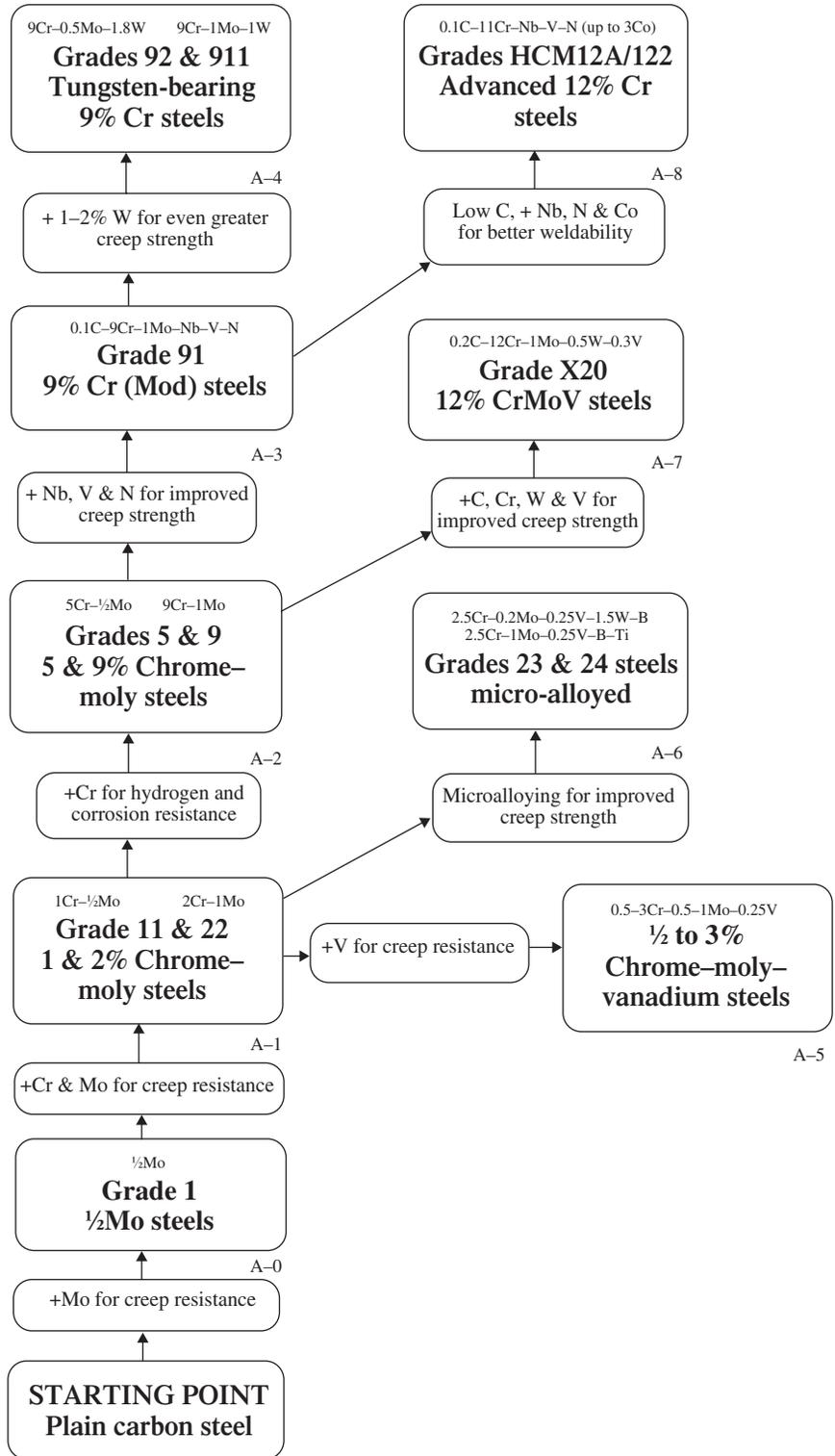
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Group A

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# **Creep-resisting low-alloy steels**



Group A: Creep-resisting low-alloy steels.

# Introduction

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The starting point for Group A is plain carbon steel with a carbon content of about 0.2% and essential deoxidants such as manganese and silicon. This composition gives a pearlitic structure of modest strength designed primarily for use at ambient temperatures. This group demonstrates the effect of increasing alloy content to improve high-temperature creep performance. It illustrates the evolution from a very simple steel with 0.5% molybdenum, designed for service up to about 450°C, through to the latest 9 and 12% chromium–molybdenum alloys with complex microalloying, designed for very long-term, high-pressure service at temperatures above 600°C.

Microstructures change from tempered bainite at the lowest alloy content, through to very strong, tough, tempered martensite with complex carbides and carbonitrides. The most highly alloyed grades, with 12% chromium, are at the threshold of stainlessness, but their application, rather than their composition, means that they are correctly included in this group.

There are a number of side branches, describing steels which do not fall naturally on the main alloy branch, but which are also low-alloy high-temperature steels.

# A-0

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## 0.2% carbon, 1% manganese, 0.5% molybdenum fine-grained elevated temperature steel

Also known generically as P1 steels

### Description

This steel is a very simple and economic development of plain carbon manganese steels where the addition of only 0.5% molybdenum has a significant effect on high-temperature properties. A typical composition is:

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	C	Mn	Mo	Si	S	P	Al
Weight %	0.15	1	0.5	0.3	<0.02	<0.02	0.05

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This steel is normally supplied in accordance within one of many national and international standards, a few examples of which are given below:

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UNS	ASTM	EN
K12822	Gr. P1	1.5415
K11522		
K12821		
J12522		

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These steels are usually supplied in the normalised and tempered (N + T) condition to ensure a fine-grained microstructure with some matrix strengthening and some carbides.

### Background

Carbon manganese steels represent the most cost-effective method of alloying, to achieve reasonable strength and toughness combined with good weldability but the addition of only about 0.5% molybdenum gives some improvements in higher-temperature performance and represents the first stage in the evolution of more highly alloyed chrome-molybdenum and chrome-molybdenum-vanadium creep-resisting steels.

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## **Performance**

The addition of about 0.5% molybdenum provides a degree of matrix strengthening and a modest increase in strength over the plain carbon–manganese steels. However, the real improvement comes in achieving and retaining tensile strength and providing reasonably good creep strength at temperatures up to about 450°C. This is still well below that required for modern steam-generating plant but represents a useful improvement over carbon–manganese steels at a very modest cost premium. The molybdenum content also enhances resistance to hydrogen attack.

## **Applications**

These steels are used primarily for the manufacture of process vessels and associated pipework in chemical and oil refinery process plant. They are used for plant operating at modest temperatures often with hydrogen present and offer good creep resistance and ductility at temperatures not exceeding 400–450°C. For more demanding conditions, higher-alloyed steels would be used.

# A-1

## 1¼% chromium-½% molybdenum and 2¼% chromium-1% molybdenum creep-resisting steels

Also known generically as Grades P11 or P12 and P21 or P22

### Description

These steels are plain chromium–molybdenum creep-resisting steels with no additional strong carbide formers. Typical compositions are:

		C	Mn	Si	S	P	Cr	Mo
Weight %	P11	0.15	0.5	0.3	<0.02	<0.02	1.25	0.5
	P22	0.07	0.6	0.3	<0.02	<0.02	2.25	1

The steels are normally supplied in accordance within one of many national and international standards, a few examples of which are given below:

	UNS	ASTM	EN
P11	K11597	Gr. 11 & 12	1.7355
	J12072		
P22	K21590	Gr. 21 & 22	1.7383
	J21890		

These steels are typically supplied in the normalised and tempered condition and, if subjected to fabrication and welding are usually retempered at about 690 °C. The resultant microstructure is tempered medium carbon bainite with no retained ferrite.

### Background

These plain chrome–moly creep-resisting steels are the simplest of the true creep-resisting steels in this group. They rely on matrix strengthening from the chromium and molybdenum and on the same elements to provide carbides for grain boundary and dislocation pinning. These steels were developed in the early part of the 20th century and were the ‘workhorse’ steels used in modern fossil-fuelled power generation plant for many decades until the development and introduction of P91 steels during the late 1970s (A-3).

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## Performance

These steels are designed for very long-term service in the creep range at temperatures up to about 560 °C and some components and pipework have been in service for more than 250 000 hours (>30 years). However, their creep strength is quite modest when compared with modern advanced steels and this has resulted in the use of very thick-walled components in order to give the necessary performance with high temperatures and pressures. For example, power station main steam pipes often have a wall thickness in excess of 100 mm with obvious implications in terms of fabrication, repair, handling and support costs.

## Applications

The main areas of application are steam-generating plant including piping, turbine casings, steam chests, valve bodies and boiler superheaters.

These steels are also widely used in oil refineries and provide good corrosion resistance against sulphur-bearing crude oils at 250–450 °C. They are also used in the chemical and petrochemical industries because of their resistance to hydrogen attack and blistering at temperatures up to about 450 °C. Typical applications are hydrocrackers, coal liquefaction plant and ammonia pressure vessels.

These steels and welded joints can suffer from temper-embrittlement after long periods of high-temperature service, which results in embrittlement and a risk of low-temperature brittle fracture in some process plant. Special grades of steel and weld metals, with low residuals such as phosphorus and arsenic, are used to reduce the risk of serious failures.

## A-2

### 5% chromium- $\frac{1}{2}$ % molybdenum and 9% chromium-1% molybdenum creep-resisting steels

Also known generically as Grades P5 and P9

#### Description

These steels are plain chromium–molybdenum creep-resisting steels with no additional strong carbide formers but with significantly more chromium than P11 and P22. Typical compositions are:

		C	Mn	Si	S	P	Cr	Mo
Weight %	P5	0.1	0.5	0.5	<0.02	<0.02	5	0.5
	P9	0.1	0.5	0.5	<0.02	<0.02	9	1

The steels are normally supplied in accordance within one of many national and international standards, a few examples of which are given below:

	UNS	ASTM	EN
P5	K41545	Gr. 5	1.7373
	J42045		
P9	K50400	Gr. 9	1.7388
	J82090		

These steels are usually supplied in the normalised and tempered condition and, if subjected to fabrication and welding are usually retempered at about 730°C and 760°C respectively. The resultant microstructure is tempered medium carbon bainite and martensite–bainite with no retained ferrite.

#### Background

These steels rely on matrix strengthening from the chromium and molybdenum and on the same elements to provide carbides for grain boundary and dislocation pinning. In this respect they do not offer major benefits over P22 types. However, the increased chromium content provides additional corrosion resistance and protection against high-temperature hydrogen

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attack and blistering. The steels were developed in the early part of the 20th century and are most widely used in oil refineries and similar plants. The 9%Cr steel formed the basis for the more advanced creep-resisting steel P91 (A-3).

## **Performance**

These steels are designed for long-term service in the creep range at temperatures up to about 600°C in superheated steam, hot hydrogen gas and high-sulphur crude oils.

## **Applications**

The main areas of application are in oil refineries. Most modern refineries have heat exchangers, pipework and vessels made from Grade 5 steel where resistance to high-sulphur crude oils and hot hydrogen is required. A more recent and common application is in the fabrication of desulphurisation plants used for the production of clean low-sulphur petrol and diesel fuels.

Grade 9 steel is not so widely employed, but it has been used for power plant boiler superheaters as an intermediate grade between the lower alloyed P22 and higher alloyed stainless grades. A limited number of oil refineries, particularly those operating at higher temperatures and producing high-grade metallurgical carbon as a by-product, use Grade 9 steel to provide improved corrosion and hot hydrogen resistance at somewhat higher temperatures.

# A-3

## Modified 9% chromium, 1% molybdenum creep-resisting steel

Also known generically as Grade P91

### Description

P91 is essentially a 0.1% carbon, 9% chromium, 1% molybdenum steel, modified with controlled additions of vanadium, niobium and nitrogen to give long-term, high-temperature creep strength. A typical composition is:

	C	Mn	Si	S	P	Cr	Ni	Mo	Nb	V	N
Weight %	0.1	0.5	0.3	<0.01	<0.02	9	0.1	1	0.08	0.2	0.05

The steel is normally supplied in accordance within one of the following specifications:

UNS	ASTM	EN
K90901	Gr. 91	1.4903
J84090		

This steel is supplied in the normalised and tempered condition and, if subjected to fabrication and welding is usually retempered at about 760°C. The resultant microstructure is tempered medium carbon martensite with little or no retained ferrite.

### Background

'Super 9 chrome' alloys were initially evaluated for power boiler use in the late 1950s; however, the present generation of P91 steels arose from a development programme in the USA. In 1974 the Oak Ridge National Laboratory (ORNL) in conjunction with Combustion Engineering initiated a project to develop a 9%Cr–1%Mo alloy steel that combined the advantages of the existing 9%Cr and 12%Cr steels with improved weldability.

### Performance

The advantages of P91 steels over established steels such as P22 (2%Cr–1%Mo) and X20 (12%CrMoV) is clearly illustrated by comparing the

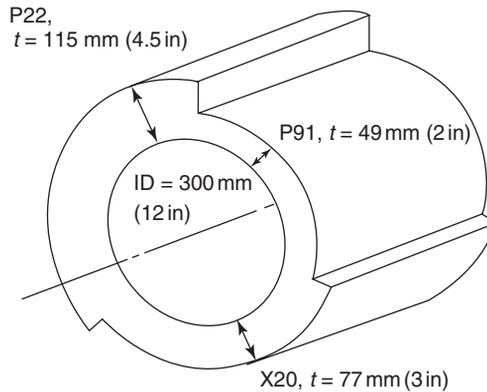


Figure 1 Pipe thicknesses for P91 steel compared with those of P22 and X20 steels, for the same operating conditions.

relative steam pipe wall thicknesses required for a set of typical operating conditions and equivalent service life (temperature 600 °C, pressure 30 MPa, design life 100 000 hours) (Fig. 1).

## Applications

The first set of 9%Cr–1%Mo (modified) tubes were installed in superheater sections in May 1980, replacing type 321 stainless steel tubing. By 1983 the steel was recognised for tubing by the American Society for Testing and Materials (ASTM) and for piping by the ASTM and the American Society of Mechanical Engineers (ASME) in 1984.

By the mid-1980s, UK interest in the material was developing and the former Central Electricity Generating Board (CEGB) established a programme that led to the installation of replacement steam headers in P91 at a major coal-fired power station in 1989.

In the 1990s, P91 became the material of choice for the repair and upgrading of existing power stations and for the construction of new units throughout the world. The main areas of application in coal-fired power stations are headers, main steam pipes and turbine casings. It is also used in the many steam lines that are an integral part of modern gas-fired combined cycle power plants. It is in all such items that the major benefits arising from reduced wall thicknesses, reduced weights and consequent cost savings can be realised. Higher operating temperatures and pressures can also lead to improvements in thermal efficiency and reduced carbon dioxide emissions. This is a major driver behind the use of P91 and other, more advanced, creep-resisting steels.

# A-4

## Modified 9% chromium, 1% molybdenum creep-resisting steel with tungsten

Also known generically as Grade 92/NF616 and E911

### Description

These are essentially 0.1% carbon, 9% chromium, molybdenum steels, modified with controlled additions of tungsten, vanadium, niobium and nitrogen to give exceptional long-term, high-temperature creep strength. Typical compositions in weight % are:

	C	Mn	Si	S	P	Cr	Ni	Mo	W	Nb	V	N	B
<b>P92/NF616</b>	0.1	0.5	0.3	<0.01	<0.01	9	0.1	0.5	1.7	0.06	0.2	0.05	0.003
<b>E911</b>	0.1	0.8	0.3	<0.01	<0.01	9	0.1	1	1	0.05	0.2	0.05	-

The steels are normally supplied in accordance within one of the following specifications:

	UNS	ASTM	EN
<b>P92/NF616</b>	K93640	Gr. 92	
<b>E911</b>			X11CrMoWVNb 9 1 1

These steels are supplied in the normalised and tempered condition and, if subjected to fabrication and welding are usually retempered at about 760°C. The resultant microstructure is tempered martensite with little or no retained ferrite.

### Background

These steels are developments of P91 with additions of tungsten to provide very stable carbides and further improve creep strength. P92 was originally developed in Japan in the 1990s as NF616 and was incorporated into the ASTM and ASME code as Grade 92. In this steel the molybdenum content is reduced to 0.5% with an addition of about 1.7% tungsten.

E911 is a result of European developments, which took place over the same period; the result was a slightly different variant with molybdenum

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held at 1% and a straight addition of 1% tungsten. At the present time this steel is incorporated in the Euro Norm (EN) standards, but is not yet recognised by the ASME code.

### **Performance**

The steels are designed to operate at temperatures up to at least 600 °C and have creep rupture strengths that, it is claimed, are up to 30% greater than P91. These are relatively new steels and data, particularly on welded joints, are still being generated. Assuming that the full potential of the steels can be exploited, it should result in even greater reductions in wall thickness of high-pressure components with consequent weight, fabrication and cost savings.

### **Applications**

The first commercial use of these steels took place in Europe only around the year 2000 and the range of applications is still being developed and explored. The main area of use is in the construction of the most modern high-temperature, high-efficiency fossil-fuelled power stations. Probable components are headers, main steam piping, boiler tubes, turbine casings, steam chests and valves. There may also be future applications in oil refining, petrochemical, coal liquefaction and gasification plants where significant reductions in wall thickness of high-temperature, high-pressure vessels may be possible.

## A-5

### $\frac{1}{2}$ -3% chromium, $\frac{1}{2}$ -1% molybdenum, $\frac{1}{4}$ % vanadium creep-resisting steels

Also known generically as CrMoV types

#### Description

These steels are chromium–molybdenum creep-resisting steels with a range of chromium and molybdenum contents plus the addition of about 0.25% vanadium as a strong stable carbide former. Some grades have titanium and boron additions or niobium and calcium. Typical compositions are:

	C	Mn	Si	S	P	Cr	Mo	V
Weight %	0.1	1	0.3	<0.02	<0.02	0.5-3.5	0.5-1	0.25

A number of these steels are vanadium-containing variants of well-established chrome–moly creep-resisting steels. They have not yet been allocated Unified Numbering System (UNS) and EN numbers but are used under ASME code cases as follows:

- 2.25Cr1Mo0.25V – code case 2098-1
- 3Cr1Mo0.25V Ti B – code case 1961
- 3Cr1Mo0.25V Nb Ca – code case 2151 (ASTM Gr. F3V)

The steels are usually supplied in the normalised and tempered condition and, if subjected to fabrication and welding are usually retempered at about 700°C. The resultant microstructure is tempered medium carbon bainite with vanadium carbides and no retained ferrite.

#### Background

Creep-resisting steels containing vanadium have been used throughout the second half of the 20th century as an economic alternative to the more highly alloyed types. Fossil-fuelled power stations have taken advantage of the good long-term creep life of  $\frac{1}{2}$ %Cr– $\frac{1}{2}$ %Mo– $\frac{1}{4}$ %V and  $1\frac{1}{4}$ %Cr–1%Mo– $\frac{1}{4}$ %V alloys, particularly in main steam lines, valve chests and turbine casings.

More recently, interest has focused on the higher alloy types, particularly those with 3% chromium, 1% molybdenum and  $\frac{1}{4}$ % vanadium in order to give high-temperature creep properties suitable for use in high-hydrogen

atmospheres. Development of the latest grades started in the mid-1980s and still continues.

## **Performance**

These steels are designed for very long-term service in the creep range at temperatures up to about 580 °C either with high-pressure steam or high-pressure hydrogen.

The lower-alloy grades tend to be used under steam conditions and show a reasonable degree of corrosion/erosion resistance in superheated steam. However, there is a marked improvement in high-temperature rupture strength when the chromium content exceeds 2¼% and the 3% chromium grades are usually selected for this type of service.

## **Applications**

The main areas of application for the lower-alloyed types are steam-generating plant including piping, turbine castings, steam chests and valve bodies. However, many of these applications have largely been superseded by more modern alloys such as P91 (A-3).

The main application for the higher chromium types is in the manufacture of highly safety-critical hydrocracker and hydrotreater vessels used in oil refineries. Hydrocrackers are used to crack heavy oils with hydrogen at high temperatures in the range 450–600 °C and pressures up to 100 bars, in order to produce light fuels. To withstand such operating conditions, vessels can have a wall thickness up to 250 mm and can weigh up to 1000 tonnes!

Similar conditions are encountered in hydrotreaters, which are used to remove sulphur in the production of clean, low-sulphur petrol and diesel fuels. High temperatures and pressures are again required in order to minimise coke formation.

# A-6

## 2¼%-2½% chromium plus alloying creep-resisting steels

Also known generically as Grades T23 and T24

### Description

These steels are low chromium (~2%) steels with controlled additions of strong carbide formers and boron to give much improved high temperature creep strength when compared with Grade 22, and at modest additional alloying cost. Typical compositions are:

		C	Mn	Si	Cr	Mo	W	Nb	V	B	Ti
Weight %	T23	0.06	0.5	0.3	2.2	0.15	1.6	0.05	0.25	0.002	-
	T24	0.07	0.5	0.3	2.25	1	-	-	0.25	0.004	0.07

As relatively new steels, they have not yet been allocated UNS and EN numbers. However they do have ASTM grades.

	ASTM
T23	A213 Gr. T23 (code case 2199)
T24	A214 Gr. T24

They are usually supplied in the normalised and tempered condition and, if subjected to fabrication and welding are usually retempered at about 730°C, as required by the ASME code case for T23. However, these steels are often used for relatively thin-walled boiler tubes and are usually put into service without post-weld heat treatment (PWHT). The microstructure is tempered medium carbon bainite with no retained ferrite.

### Background

T23 and T24 are modern (late 1990s) developments of the well-established 2¼%Cr-1%Mo (T22) steel and are closely related to the CrMoV steels described in A-5.

In the case of T23, the molybdenum is virtually eliminated and replaced by significant amounts of the strong carbide formers, namely tungsten,

vanadium and niobium. There is also a very small controlled addition of boron.

With T24, the molybdenum is retained at 1% with a modest addition of vanadium and controlled small additions of titanium and boron, which have a synergistic effect in stabilising the microstructure. Carbon is also maintained at the relatively low level of about 0.07% to improve weldability and thin-walled tubes can be welded without preheat.

## **Performance**

These steels are designed for very long-term service in the creep range at temperatures up to about 600°C and it is claimed that rupture strength is twice that of Grade 22 (A-1) and comparable with that of the modified 9%Cr-1%Mo modified type Grade 91 (A-3). While most data have been generated for relatively thin-walled boiler tubes, work is now in hand to expand the range of applications and in particular to explore the potential for thicker-walled welded pipework.

## **Applications**

The main area of application at the present time is in the fabrication of boiler waterwalls in ultra-supercritical (USC) boilers in fossil-fuelled power stations. These are designed to operate at very high steam temperatures, in excess of 650°C, with consequent significant improvements in overall thermal efficiency and reductions in emissions and pollutants. These steels have only recently been developed and a wider range of applications is still being validated.

# A-7

## 12% chromium, molybdenum, vanadium creep-resisting steel

Also known generically as Grade X20

### Description

X20 is essentially a 0.2% carbon, 12% chromium, 1% molybdenum steel, with significant controlled additions of vanadium to give long-term, high-temperature creep strength. A variant of this grade also contains 0.5% tungsten for further creep strength. Its typical composition is:

	C	Mn	Si	S	P	Cr	Ni	Mo	V	(W)
Weight %	0.2	0.5	0.3	<0.02	<0.02	12	0.5	1	0.3	(0.5)

The steel is normally supplied in accordance within one of the following specifications:

UNS	AISI	EN
-	Type 422	X20CrMoV 12 1 (1.4922) with tungsten (1.4935)

X20 is supplied in the normalised and tempered condition and, if subjected to fabrication and welding is usually retempered at about 750°C. The resultant microstructure is tempered moderately high carbon martensite with little or no retained ferrite.

### Background

This steel is designed for critical heat- and creep-resisting service at temperatures up to at least 550°C. It is widely used in the worldwide power generation industry for steam turbine blades. In some countries, particularly in Central Europe and Germany, it has been exploited, throughout the second half of the 20th century, for other components and steam pipes. The steel has to be welded with care and with special procedures to avoid the risk of hydrogen cracking and this treatment adds to the cost and complexity of fabrication. More advanced creep-resisting steels with better properties and improved weldability, such as P91 (A-3), have largely superseded this steel for fabricated components.

There are a large number 12% chromium steels both proprietary and referenced in specifications such as those of the American Iron and Steel Institute (AISI). One of the more well known is Jethete M152, which is similar to X20 but has reduced carbon, increased nickel, increased molybdenum and controlled nitrogen additions of about 0.3%.

## **Performance**

Steel X20 is roughly mid-way in creep performance between P22 and P91. However the chromium content of 12% makes the steel virtually 'stainless' in terms of corrosion resistance and this is beneficial in steam corrosion/erosion and some fireside environments. In this respect it is superior to P22 (A-1) and somewhat better than P91 (A-3).

## **Applications**

The main application area for these steels is in the power generation industry. They are also used in some specialised petrochemical components where the combination of high creep strength and corrosion resistance can be utilised. They are used as shafts and impellers where the corrosive environment is not too severe.

However, the main area of application is in turbine and diaphragm blades. They are more suitable for the high and intermediate pressure stages of steam turbines where there is less risk of wet steam erosion. Higher chromium grades with levels up to about 14% are often used in the low-pressure stages.

# A-8

## Modified 12% chromium, 0.5% molybdenum, 2% tungsten creep-resisting steel

Also known generically as Grade 122 and HCM12A

### Description

P122 is a further development of P91 and P92 with a higher chromium content and balanced additions of strong and stable carbide formers such as molybdenum, tungsten, vanadium and niobium. Like other modern high-temperature low-alloy steels, there is also a controlled nitrogen addition of about 0.06%. A typical composition is:

	C	Mn	Si	S	P	Cr	Ni	Mo	W	Nb	V	N
Weight %	0.1	0.6	0.3	<0.01	<0.02	11.5	0.3	0.5	2	0.06	0.2	0.06

The steel is normally supplied in accordance within one of the following specifications:

UNS	ASTM
K92930	A213 T122 (seamless tubes) A335 P122 (seamless pipes).

This steel is supplied in the normalised and tempered condition and, if subjected to fabrication and welding is usually retempered at about 760°C. The resultant microstructure is tempered medium carbon martensite with little or no retained ferrite.

### Background

This steel can be considered as yet a further evolutionary development of the P91 and P92 types. It was originally developed by Sumitomo Metal Industries within the last decade of the 20th century and was designated as HCM12A. It was recently included in the ASME code with generic designation of grade P122. It has similar creep strength to alloys such as P92 and E911 but the higher chromium content is claimed to give improved oxidation resistance at very high steam temperatures.

On-going steel developments are now looking at non-austenitic steels that are suitable for service up to 650°C to give further improvements in the thermal efficiency of ultra supercritical (USC) power plants. One of the new steels, designed for boiler applications, contains about 12% chromium, 2.5% tungsten and 2.5% cobalt, the addition of cobalt preventing the retention of delta ferrite in the microstructure. Variants of these steels are also used for turbine rotors.

## **Performance**

At 600°C the allowable stresses for P122 are about 30% greater than for P91, permitting further reductions in pressure component wall thickness with consequent reductions in thermal losses, weights and costs. Creep performance is comparable with P92 and E911 at temperatures up to about 650°C, but the increased chromium content gives improved oxidation and erosion performance at the very high steam temperatures encountered in USC power plants.

## **Applications**

The application of these steels is still fairly limited and to some extent is governed by lack of reliable data covering the long-term creep performance of weld metals and welded joints. Development work is in currently underway and it is anticipated that these advanced steels will soon begin to be used for USC power plant boilers, reheaters, superheaters and turbine rotors. It is also expected that they will be exploited in the most modern combined cycle power plants and in future generations of coal gasification units.