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ALLOY STEEL TUBE

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My invention relates to ferrous alloys. It pertains especially to ferritic alloy steels for high temperature service, though it is not necessarily limited thereto.

5 In the prior art of alloy steel, the term "heat resisting" has been used somewhat loosely to indicate resistance to corrosion or scaling at high temperatures. Various types of alloy steels have been suggested for this purpose and one class of
10 such steels is known as aluminum steels, because of the fact that they contain substantial percentages of aluminum. The use of such aluminum steels has been relatively limited. One reason is that they show a tendency towards excessive
15 piping. Another reason is that the surfaces of these aluminum steels are generally poor, due to drossing. These aluminum steels are sluggish in casting.

Some workers in the art have appreciated the
20 importance of resistance to creeping at high temperatures. Thus, it is generally recognized in the prior art that molybdenum is the element most effective to impart high creep resistance to alloy steel. Tungsten will also impart creep
25 resistance to steel, though not so effectively as molybdenum.

The percentages of these elements normally used ranges from .25 to .75 per cent for molybdenum and from .50 to 1.50 per cent for tungsten. For some classes of service, such as valve
30 steels, molybdenum and tungsten are sometimes used together, in total percentages up to 7 per cent, though normally the total percentage of these elements used does not exceed 4 per cent,
35 with the two elements present in about equal proportions.

While tungsten and molybdenum are quite effective for the purposes indicated, they are relatively costly. Thus, their use results in the
40 production of steels which are undesirably expensive. Hitherto, little or no success has been had in the production of ferritic alloy steels possessing adequate creep resistance as well as adequate corrosion resistance without the use of some such
45 material as those mentioned above.

One of the objects of this invention is to provide a steel for high temperature service which will have adequate creep resistance, adequate corrosion resistance and mechanical properties
50 adequate to meet the requirements commonly encountered under conditions of high temperature service.

Another object of this invention is to produce a steel of the type indicated which will possess
55 the properties indicated and which will also be

capable of manufacture at a relatively low cost.

This application is a continuation in part of my application upon Ferrous alloys, Serial No. 81,338, filed May 2, 1936.

My invention resides primarily in the fact that
5 I have found it possible to obtain substantially as good creep resistance in ferritic alloy steels by substituting phosphorus for a part of the molybdenum or tungsten usually considered necessary to insure adequate creep resistance. My
10 investigations show that the limitations on the use of phosphorus for the improvement of the high temperature properties of steel are governed by the types of steel employed. The upper limit
15 of phosphorus in steel is set by the appearance of brittleness and its retention at high temperatures. I have used as much as 1.0 per cent of phosphorus, depending upon the carbon and alloy
20 content, before the steels become unworkable at some elevated temperatures. I find that I may add from 0.08 per cent to 1.5 per cent phosphorus to steels, containing from traces up to 0.9 per
25 cent carbon, for high temperature service in order to improve their high temperature properties and creep-resistance properties. I prefer to use from 0.08 per cent to 0.60 per cent phosphorus in alloy grades of steel. The latter steels
30 may contain, besides carbon and the usual incidental impurities, such alloying elements as nickel, cobalt, molybdenum, silicon, titanium, tungsten, chromium, copper, vanadium, colum-
35 bium, zirconium and manganese, these alloying elements being used either singly or in combination and in such quantities as not to exceed a total alloy content in the steel of 30 per cent.

Where it has been customary previously to use from .25 to .75 per cent molybdenum in order to obtain adequate creep resistance in some chromium-bearing steels, I have found that the
40 upper limits of required molybdenum may be lowered substantially by increasing the phosphorus content. Thus, I have found that an alloy steel with 1 per cent of chromium containing .20 per cent molybdenum and .15 per cent phosphorus will give results, from the standpoint of
45 creep resistance, substantially equivalent to a steel containing 1 per cent of chromium, .50 per cent molybdenum and .03 per cent phosphorus.

The preferred composition of my new alloy is from about 0.08 per cent to 0.60 per cent phosphorus, from .10 to .75 per cent molybdenum with
50 the balance chiefly iron and chromium. However, a substantially equivalent alloy may be produced by the use of from 0.08 per cent to 0.60 per cent phosphorus, from 0.20 to 1.50 per cent
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tungsten with the balance chiefly iron and chromium.

However, it should be understood that it is within the scope of my invention to provide an alloy containing from 0.08 per cent to 1.5 per cent phosphorus, from .10 to .75 per cent molybdenum and the balance chiefly iron and chromium. Likewise, it is within the scope of my invention to provide an alloy containing from 0.08 per cent to 1.5 per cent phosphorus and from 0.20 to 1.50 per cent tungsten and the balance chiefly iron and chromium.

Novel alloy steels which I have produced containing both phosphorus and molybdenum that have been tested for creep resistance along with phosphorus-containing and molybdenum-containing steels are illustrated by the following table:

Specimen No.	Chemical composition				Creep-strength properties			
	C, per cent	Cr, per cent	P, per cent	Mo, per cent	Test temp., ° F.	Load lb./sq. in.	Duration of test, hours	Rate of deformation percent/hour at 1,000 hours
K-20	0.40	-----	0.012	None	850	10,000	1,030	0.00054
1053	0.10	1.00	0.20	None	850	12,000	1,060	0.00001
1210	0.10	1.00	0.03	0.20	850	12,000	1,130	0.00001
1211	0.10	1.00	0.50	None	950	12,000	1,175	0.00005
1212	0.10	1.00	0.03	0.50	950	12,000	1,010	0.00001
1892	0.11	-----	0.17	0.21	950	12,000	1,175	0.000075
1747	0.17	0.92	0.17	0.20	950	12,000	1,410	0.000012
1750	0.18	2.38	0.17	0.21	850	20,000	1,375	0.00001
1750	0.18	2.38	0.17	0.21	850	28,000	1,685	0.000015
877	0.07	-----	0.21	None	850	12,000	1,510	0.000075
1052	0.10	-----	0.35	None	850	12,000	1,050	0.00001
1734*	0.12	0.97	0.32	None	850	20,000	1,375	0.000055

* Contained 1.05 percent silicon and 0.37 percent copper.

The resistance to creep is expressed as the rate of deformation in per cent per hour at 1,000 hours.

This table shows that on increasing the phosphorus content of carbon steel from a low value to 0.21 per cent and to 0.35 per cent the rate of deformation or creep was reduced materially; thus one can clearly see the effect on creep-resistance of phosphorus in steels. The chromium-molybdenum steels were useful to compare the effect of phosphorus and an equal amount of molybdenum in alloy steels.

The 1 per cent chromium, 0.2 per cent molybdenum steel, 1210, showed slightly better creep-resistant properties than the 1 per cent chromium, 0.2 per cent phosphorus steel, 1053, in that its rate of deformation is slightly less than 0.00001 per cent per hour. The difference in rates of deformation is very small; hence, for all practical purposes the steels may be considered to possess comparable creep resistance at 850° F.

The 1 per cent chromium steels containing either 0.5 per cent phosphorus or 0.5 per cent molybdenum were expected to show better creep resistances than the other steels, due to the additional amount of phosphorus or molybdenum contained. For this reason, tests on these steels were conducted at the same load of 12,000 lbs. per sq. in. but at the high test temperature of 950° F. At 1,000 hours steel 1211, containing 1 per cent chromium and 0.5 per cent phosphorus, showed a rate of deformation of about 0.00005 per cent per hour, while steel 1212, containing 1 per cent chromium and 0.5 per cent molybdenum, showed a rate of about 0.00001 per cent per hour. However, the rate for the 1 per cent chromium, 0.5 per cent phosphorus steel was steadily diminishing as the test progressed and it is probable that had the deformation continued strain-hardening would

have lowered the rate of deformation sufficiently to more nearly approximate that of the 1 per cent chromium, 0.5 per cent molybdenum steel. The behavior of the two steels indicated that steel containing 0.5 per cent molybdenum has more ability to strain-harden at 950° F. than does steel with 0.5 per cent phosphorus, but that over a very long period of time the rate of deformation of steel containing equal amounts of either of the two elements becomes very nearly the same.

While, from the standpoint of creep resistance, the benefits of phosphorus in steel when employed alone or with chromium were definitely established, it remained to evaluate the effect of combining phosphorus with molybdenum or with tungsten, the two elements most effective to give better creep resistance to steels for services at elevated temperatures. I, therefore, prepared

and tested steels having various combinations of phosphorus and molybdenum with and without chromium and have found it both possible and practical to substitute phosphorus for some of the molybdenum without reducing the creep resistance of the steels. Steel 1747 contained 0.92 per cent chromium, 0.17 per cent phosphorus, and 0.20 per cent molybdenum, and after testing at 950° F. and 12,000 lbs. per sq. in. for a period extending over 1,000 hours, I found that its creep resistance was almost identical with that of steel 1212 containing 1.0 per cent chromium and 0.50 per cent molybdenum. The low molybdenum in conjunction with phosphorus in steel 1747 was, therefore, almost equally as effective toward imparting creep resistance as the 0.50 per cent molybdenum was in steel 1212. As the cost of molybdenum is six times that of phosphorus, I have discovered a simple and practical way to materially reduce the alloy cost of steels which are used for their creep resistance at elevated temperatures that comprises replacing some of the costly molybdenum with the less expensive phosphorus. Within alloy limits specified in my invention, I may replace a given percentage of molybdenum with an equal percentage of phosphorus without materially affecting the creep properties.

Since tungsten is two times as expensive as molybdenum, it will be seen that an even greater reduction in cost is possible by the substitution of phosphorus for a portion of the tungsten in order to obtain substantially equivalent creep resistance.

The possibility of utilizing phosphorus in a ferritic chromium steel containing up to 25 per cent of chromium and either from 0.10 to 0.75 per cent molybdenum or from 0.20 to 1.50 per cent tungsten to improve the high-temperature

creep resistance properties is thus clearly demonstrated. The steels may contain besides carbon, chromium, phosphorus, molybdenum, or tungsten, and the usual incidental elements, such as nickel, cobalt, silicon, titanium, copper, vanadium, columbium, zirconium and manganese, the latter alloying elements being used either singly or in combination but in such quantities as not to destroy the ferritic nature of the steels, or to exceed a total content in the steels of 5 per cent.

It will be seen from the above that I have been able to produce an alloy steel without the use of aluminum but which is nevertheless a heat resistant steel wherein adequate creep resistance is attained by the substitution of phosphorus for a substantial part of the molybdenum normally relied upon to accomplish this result. Thus, I have avoided the drawbacks normally arising from the use of substantial quantities of aluminum in such alloy steels and, at the same time, have been able to reduce the cost of steels of this type. The use of chromium in the percentages indicated insures that the steel will have adequate resistance to scaling, as well as adequate creep resistance.

The alloy which I have described is particularly useful for making oil-cracking still tubes and oil still castings. Such tubes and oil still castings when in service are subjected to high pressures at high temperatures. Therefore, it is very important that the alloys used in making such tubes and oil still castings be of such a nature that the creep-resistant properties are adequate at the high temperatures and high pressures to which the tubes and oil still castings are subjected in the cracking process. The phosphorus-bearing alloys, containing from 0.08 per cent to 1.5 per cent phosphorus, which I have described will have adequate creep-resistant properties at the high temperatures and high pressures to which the still tubes and oil still castings are subjected in the cracking process. Furthermore, the alloy has other high temperature properties, such as heat and scale-resistance, which render it particularly suitable for use in still tubes and

oil still castings. When the still tubes and oil still castings are used at temperatures above 850° F. it is desirable that the alloy contain one or more of such elements as chromium, molybdenum, vanadium, zirconium and tungsten to offset the diminution in the effect of the phosphorus at temperatures above approximately 850° F.

Other advantages will appear from the preceding description and the following claims.

Having thus described my invention, what I claim is:

1. An alloy steel tube for use under conditions requiring scaling resistance and high creep resistance at high temperatures and high pressures, said tube being composed of an alloy consisting essentially of carbon in amounts up to 0.9 per cent, phosphorus in amounts from 0.08 to 1.5 per cent, chromium in effective amounts up to 25 per cent, molybdenum in amounts from .10 to .75 per cent, and the balance substantially all iron and incidental impurities, the phosphorus cooperating with the molybdenum to impart creep resistance at least equal to that imparted to similar alloys by substantially larger amounts of molybdenum when used with phosphorus in amounts less than 0.05 per cent.

2. An alloy steel tube for use under conditions requiring scaling resistance and high creep resistance at high temperatures and high pressures, said tube being composed of an alloy consisting essentially of carbon in amounts up to 0.9 per cent, phosphorus in amounts from 0.08 to 1.5 per cent, chromium in effective amounts up to 25 per cent, at least one alloying ingredient from the class consisting of molybdenum and tungsten in a total amount from 0.10 to 1.5 per cent, and the balance substantially all iron and incidental impurities, the phosphorus cooperating with the said alloying ingredient to impart creep resistance at least equal to that imparted to similar alloys by substantially larger amounts of said alloying ingredient when used with phosphorus in amounts less than 0.05 per cent.

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