

UNITED STATES PATENT OFFICE

2,123,144

APPARATUS FOR ELEVATED TEMPERATURE SERVICE

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No Drawing. Application May 5, 1936,
Serial No. 77,969

4 Claims. (Cl. 196—133)

This invention relates to apparatus for elevated temperature service in carrying highly heated liquids and gases under pressure.

Modern high temperature steam generating equipment and apparatus used for oil refining and hydrogenation and in the polymerization of gases require a tubular heater which will withstand long continued use under oxidizing and corroding conditions while subject to high temperatures and pressures. The tubes and other parts in order to be suitable for such service must retain good strength under the conditions of high temperature and high pressure to which they are subjected, and they should retain ductility and have a high creep strength under such conditions and be highly resistant to oxidation at high temperatures and to corrosion by the furnace gases and oil and oil products, steam and other vapors, and should to a high degree be free from tendency toward embrittlement as a result of long continued heating.

Tubes of the well known 18-8 iron-chromium-nickel alloy have been used with great success for cracking very corrosive oils at high temperatures and for superheating steam, but the high cost of this alloy has limited their use to only the most severe conditions of operation. Much cheaper ferrous alloys, such as the 4 to 6 chromium alloy, have also been used to a considerable extent by the oil refining industry where the conditions of operation are less severe, but tubes of this alloy are not suitable for use at the higher temperatures which are withstood by alloys containing larger amounts of chromium or in the cracking, etc., of very high sulphur corrosive oils due to the short life of parts made of this alloy even as compared to its lower cost.

The object of the present invention is to provide tubes and other apparatus parts which will satisfactorily meet all the requirements above referred to and the cost of which shall be much less than the cost of similar parts made of the 18-8 iron-chromium-nickel alloy, and which, because of their comparatively low first cost and their long life in service under even very severe conditions of operation, will be more economical to use than similar parts of other alloys heretofore used, and while possessing to a large degree the advantages even of the more expensive alloys are without certain undesirable qualities which are

found in both the more expensive and the cheaper alloys heretofore used.

To these ends, tubes and other containers according to the invention are made of a ferrous alloy containing from 8 to 10.5 percent of chromium, with from about 1 to not over about 2.5 percent of molybdenum, and not over .20 percent carbon. Such an alloy has to a high degree the properties and characteristics to meet all the requirements above referred to. In its oxidation and corrosion resistance, in its strength and creep value and retention of ductility at elevated temperatures up to about 1300° F., and in its freedom from embrittlement, it shows values not greatly less than other alloys which are more costly.

The corrosion resistance of the alloy is far superior to that of the 4 to 6 percent chromium steel and in this respect approximates that of the 18 chromium 8 nickel alloy, and its oxidation resistance is also far superior to that of the 4 to 6 chromium alloy and is sufficient for extended service at a maximum temperature of 1300° F. It retains good ductility at high temperatures up to its transformation temperature, and tubes composed of it will bulge prior to rupture, giving warning of impending failure. In this respect the alloy acts like carbon steel and the 4 to 6 percent chromium steel, and not like the 18 chromium 8 nickel alloy which is liable to rupture abruptly on overheating. It is also free from deleterious carbide precipitation which sometimes renders the 18-8 alloy subject to intercrystalline corrosion and weakness through precipitation of chromium carbide at the grain boundaries.

An especially noteworthy characteristic of the alloy which is of primary importance in parts which have to withstand pressure at high temperatures is its retention of strength at high temperatures. I have discovered that a remarkable improvement in the strength of the alloy at the high temperatures for which the articles of the invention are intended results from the addition of from 1 to 2 percent of molybdenum as compared to the addition of substantially less than 1 percent, and that only slight further increase in strength at these temperatures is obtained by increasing the molybdenum above about 2 percent. I have found that on short time elevated temperature tests, while an addition of .50 percent molybdenum to a plain iron-

chromium alloy containing about 9 percent chromium increased its ultimate strength only about 12 percent at 1000° F. and about 4½ percent at 1200° F., the addition of .98 percent molybdenum increased the strength of the same alloy about 27 percent at 1000° F. and about 23½ percent at 1200° F., and an addition of 1.85 percent molybdenum increased its strength about 57 percent at 1000° F. and about 90 percent at 1200° F., and that with 2.95 percent molybdenum the increase in strength over the plain 9 percent chromium alloy was only 57 percent at 1000° F. and only 82 percent at 1200° F.

The strength of the alloys shown by the creep or long-time flow tests which are used for determining working stresses for metals to serve in high temperature equipment is also excellent.

The carbon content of the alloy should be low, not over .20 percent, and most desirably not over .15 percent, so as to have a soft ductile metal for rolling, bending and otherwise deforming preparatory to service. In spite of its alloy content, the alloy may be made into tubes and other rolled parts, castings and forged parts, with nearly the same facility as 4 to 6 percent chromium steel, and mill practices for heating, rolling, etc., need not differ materially from those now in use for the 4 to 6 percent alloy. Low carbon is desirable also to prevent undesirable combinations of chromium and molybdenum as carbides with consequent lowering of corrosion resistance.

Structurally the alloy is normally martensitic when rapidly cooled from above its transformation temperature, unless of very low carbon content, below about .08 percent carbon. It should, therefore, be annealed, or softened, prior to use, so that operations of expanding, belling, rolling, flanging, etc., may readily be performed. In this softened condition the Brinell hardness will not exceed about 175.

If the alloy is extremely low in carbon with molybdenum and other elements toward the high side, then the gamma transformations may be partially or entirely eliminated, with the result that the alloy becomes non-hardening on air cooling or even on quenching from a high temperature. In certain cases, this is desirable, for example in welding in structures where no full annealing operation can be applied after the welding has been done. Where the composition of the alloy is such as to eliminate hardenability, the alloy becomes what may be termed an alpha-delta steel, and is no longer martensitic, that is, is free of transformation of sufficient magnitude to induce hardness. The closing up of the gamma loop also results in the advantage that the alloy shows no appreciable drop in ductility even at temperatures under which transformable steels show a sharp loss in ductility.

The steel is preferably made by the electric melting practice, so as to offset loss of valuable alloying elements and introduction of carbon. Sulphur and phosphorus should be low, consistent with good alloy steel practice, and manganese should not be over about .60 percent, as increased manganese content tends toward brittleness under long heat. Silicon may be present to the extent of about .75 percent or slightly more without harmful effect.

An alloy which has been found especially well suited for the purpose of the invention has the following composition:

	Percent	
Chromium.....	9.25	5
Molybdenum.....	1.52	
Carbon.....	.12	
Manganese.....	.46	
Silicon.....	.36	
Sulphur.....	.018	10
Phosphorus.....	.017	
Iron.....	Balance	

Alloys of the following analyses within the range described have also been found good:

	1	2	3	
	Percent	Percent	Percent	
Chromium.....	8.04	10.46	10.00	20
Molybdenum.....	1.20	1.82	1.02	
Carbon.....	.08	.17	.15	
Manganese.....	.50	.38	.54	
Silicon.....	.21	.47	.78	
Sulphur.....	.016	.022	.024	
Phosphorus.....	.017	.019	.020	
Iron.....		Balance		25

In the prevailing processes for refining petroleum, the metal temperature of the still tubes rarely, if ever, exceeds 1300° F., except in certain vapor phase processes where the pressures within the tubes are low, i. e., generally not over 100 pounds per square inch. Tubes and containers according to the present invention are well adapted for use at elevated temperatures up to 1300° F.; and the term "elevated temperature" as used herein is to be understood as meaning temperatures within the range of from about 900° F. to about 1300° F.

What is claimed is:

1. A tube or other container or part thereof for use at temperatures of the order of 1000° F. in heating fluids under high pressure, composed of an alloy substantially free of aluminum containing from 8 to 10.50 percent of chromium, from about 1.2 to about 2 percent of molybdenum, and not over 0.15 per cent of carbon, with the balance principally iron.

2. A tube or other container or part thereof for use at elevated temperatures in heating fluids under high pressure, composed of an alloy substantially free of aluminum containing from 8 to 10.50 percent of chromium, from about 1.50 to about 2 percent of molybdenum, and not over about 0.08 percent of carbon, with the balance principally iron.

3. A tube or other container or part thereof for use at elevated temperatures in heating fluids under high pressure, composed of an alloy substantially free of aluminum containing approximately 9 percent of chromium, 1.50 percent of molybdenum, and 0.12 percent of carbon, with the balance principally iron.

4. An alloy steel still tube for heating hydrocarbon oils to temperatures of the order of 1000° F., composed of an alloy substantially free of aluminum containing from 8 to 10.50 percent of chromium, from about 1.2 to about 2 percent of molybdenum, and not over 0.20 percent of carbon, with the balance principally iron.

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