Patented Feb. 20, 1951

2,542,220

UNITED STATES PATENT OFFICE

2,542,220

FERRITIC ALLOY

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No Drawing. Application October 5, 1948, Serial No. 52,983

5 Claims. (Cl. 75—123)

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The present invention deals with ferrous alloys and particularly alloy compositions designed for use where it is necessary that the alloy resist stress for extended periods of time at relatively high temperatures.

Alloys have been suggested heretofore for use in applications where it is necessary for the alloys to resist stress at moderately high temperatures in the neighborhood of 1000 to 1200° F., namely, temperatures where plain carbon steels begin to scale rapidly. One of the most widely used alloys is made with a molybdenum content of about 0.5%, the addition of which alloying constituent in the above stated amount having been found materially to contribute to the high temperature strength. In a co-pending application filed by George F. Comstock, January 15, 1948, under Serial No. 2,550, now abandoned, there has been described a titanium molybdenum steel possessing a very desirable increase in the long time high temperature strength of the known molybdenum type steels.

The continued development of high temperature devices has created an exceptional demand for high temperature strengths in steels and a demand which cannot be met by either the molybdenum type or molybdenum-titanium type steels.

It is an object of the present invention to provide a ferrous alloy possessing exceptional high temperature strength and, therefore, suitable for use in those fields demanding metals and alloys that are strong at the high temperature at which the operations are effected.

In accordance with the present invention, a ferrous alloy possessing exceptional resistance to stress for long periods of time, at temperatures in the neighborhood of 1000 to 1200° F., is provided by combining small amounts of boron, on the order of hundreds of a percent, with titanium or columbium in low carbon steel.

The following table shows the relations between the tensile strengths causing rupture of the indicated types of low carbon steel in 1000 hours at 1000 or 1100° F. and the steel of the present invention:

Type of Steel	Heat Treatment	Stress Causing Rupture in 1000 hrs., in lbs. per sq. in.	
		At 1000° F.	At 1100° F.
Plain low-carbon	Annealed	12,000	6,000
0.5% Molybdenum	do	22,000	8,000
0.5% Mo. 0.3% Ti	Normalized at 1650° F. Tempered at 1200° F.	23,000	16,000
0.3% Ti, 0.02% B	Normalized at 2100° F. Tempered at 1200° F.	45,000	
	Tempered at 1000° F.		20,000

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Steel containing as much as 0.02% boron but no titanium has been found to be very difficult to roll or forge at the usual working temperatures used therefor, because of the presence of a low-melting ternary iron-boron-carbon eutectic, which becomes liquid at such temperatures and causes the steel to separate into fragments instead of deforming. In titanium steels, however, where the carbon is fixed as titanium carbide, or in columbium steels where it is fixed as columbium carbide, thereby simulating a carbonless alloy, considerable boron content can be tolerated without seriously affecting the hot work characteristics, specifically red-shortness. The iron-boron alloy alone does not liquefy in the steel at normal rolling temperatures, and the harmful ternary eutectic cannot form.

Thus for practical reasons, to insure satisfactory hot-working quality, this new steel must contain at least four times as much titanium, or eight times as much columbium, as carbon. To avoid the necessity for the use of too much titanium, or columbium, the carbon content of the steel is held low, or around 0.03 to 0.07%. A ratio of titanium to carbon, between 5.5 and 12 has been found satisfactory, both for hot-workability and for high-temperature strength, and the titanium content, therefore, generally runs from about 0.2 to 0.7%. The boron content for best results should be between 0.01 and 0.03%, although higher values up to about 0.1% can be tolerated when the carbon is effectively stabilized or combined by titanium or columbium. With boron above 0.1%, the ductility of the steel may be adversely affected. Maganese, silicon, sulfur, and phosphorus are of no more importance in this steel than in all other steels; none of these elements need be added, but all generally occur in the steel in small amounts. Phosphorus and sulfur are not desired, and should probably be kept below 0.05%. Manganese generally runs about 0.2 to 0.4%, but may be up to 2% or more, if desired, for increasing the room-temperature strength. About 0.1% silicon is normally acquired from the ferrotitanium used; higher silicon is not necessary but it may be added up to 1%

or more, if desired, to improve scaling resistance. This steel will generally be thoroughly killed by aluminum, using about 2 to 4 pounds per ton before the titanium and boron are added, to prevent excessive loss of the titanium by oxidation.

The steel can be made readily by the basic open-hearth process, merely by the addition of the required boron and titanium in the ladle, to a low-carbon steel heat. Steel with the required low carbon content of 0.03 to 0.07% is commonly made by well-known practices. Titanium steel of this carbon content is also readily made merely by deoxidation in the ladle or furnace spout with aluminum when the heat is tapped, adding the required ferrotitanium in the ladle thereafter in the usual fashion, and covering the molten steel in the ladle with lime instead of allowing the oxidizing furnace slag to flow onto the ladle. The new titanium-boron steel can be made in the same way with an addition of ferroboron made at the same time as the ferrotitanium; or more simply by merely using as the source of titanium a ferro-alloy containing about 40% titanium, 2% boron, about 1% silicon, 0.1% or less carbon, and about 8 to 15% aluminum, which can be readily made by thermit reaction in the same way that ferrotitanium is made, except for the addition of a boron compound to the crucible charge.

This titanium-boron steel can be hardened by quenching from a temperature above about 2000° F., but is also hardenable at slower rates of cooling. This hardness is not materially decreased by tempering even at as high a temperature as 1200° F. The data in Table I illustrate these characteristics:

TABLE I

Rockwell B hardness of heat treated titanium and titanium-boron steels

	Steel No. 1	Steel No. 2
Carbon content, per cent	0.030	0.034
Manganese content, per cent	0.22	0.23
Silicon content, per cent	0.09	0.09
Titanium content, per cent	0.28	0.30
Boron content, per cent	None	0.026
Hardness after quenching in water from 2,100° F	94	101
Hardness after air-cooling from 2,100° F	64	93
Hardness, air-cooled from 2,100° F., tempered 1 hr. at 800° F	69	91
Hardness, air-cooled from 2,100° F., tempered 1 hr. at 1,000° F	65	95
Hardness, air-cooled from 2,100° F., tempered 1 hr. at 1,200° F	66	90
Hardness after slow cooling from 2,100° F	44	86

The resistance of the new titanium-boron steel to softening by tempering at 800 to 1200° F., after hardening at about 2100° F., is accompanied by a remarkable maintenance of strength when it is stressed at the same temperatures after similar hardening. The resistance of this new steel to rupture under long-continued stress at 1000 or 1100° F. is in fact far superior to that of any other low-alloy ferritic steel that has been proposed for this type of service. Comparisons with other steels in this respect are provided by the high-temperature rupture-time data in Table 2.

TABLE II

Time for rupture of various steels under constant stress at 1100° F.

Test No.	Type of Steel	Heat Treatment, °F.		Stress, Lbs. per Sq. in.	Time for Rupture, Hours	Elongation Per Cent in 2 in.
		Air-Cooled From—	Tempered, 1 hr. at—			
1	0.15% C, no alloys (B & W data)	1,550 (Annealed)		10,000	30	High
2	0.13% C, 0.5% Mo (B & W data)	1,650 (Annealed)		20,000	40	Low
3	0.03% C, 0.5% Mo, 0.3% Ti	1,650	1,200	25,000	24	35
4	0.03% C, 0.5% Mo, 0.5% Ti	2,100	1,000	25,000	48	35
5	0.03% C, 0.3% Ti, 0.026% B	2,100	1,000	25,000	Over 500	
6	0.03% C, 0.3% Ti, 0.026% B	2,100	1,000	30,000	490	20
7	0.03% C, 0.3% Ti, 0.026% B	1,900	1,000	30,000	Less than 1	35
8	0.04% C, 0.24% Ti, 0.012% B	2,100	1,200	30,000	240	21
9	0.03% C, no Ti, 0.025% B	2,100	1,000	30,000	Less than 1	80
10	0.056% C, 0.3% Ti, 0.025% B, 2.82% Cr	2,100		30,000	428	18

Comparing test No. 5 in Table II with No. 4 indicates the necessity for boron in this new steel in order to obtain exceptional resistance to stress at high temperature. A comparison of test No. 9 with No. 6 similarly indicates the necessity for titanium. The result of test No. 7 reveals the necessity for a hardening heat treatment above 1900° F. Test No. 8 shows that 0.012% boron is not too low for outstanding rupture strength at 1100° F., and also that tempering as high as 1200° F. can be tolerated without losing the great advantage in rupture strength possessed by the titanium-boron steel over titanium steel without boron as in tests No. 3 and 4. Test No. 10 shows that high rupture strength at 1100° F. is attainable in titanium-boron steel without tempering, provided the hardening heat treatment at 2100° F. is used; this is because the effect of tempering is experienced while the specimen is being heated to 1100° F. in the stress-rupture furnace before starting the test.

The new titanium-boron steel, after the heat treatment required for maximum high-temperature strength, has acceptable room temperature strength and ductility, but low notch toughness. If higher room-temperature strength is desired, such alloys as manganese, copper, nickel, etc., can be added without altering the effect of titanium and boron on the high-temperature strength.

The notch-toughness can be improved by sacrificing some of the advantage in high-temperature strength by over-tempering, as for instance in test No. 8 of Table 2, but even with the high-temperature strength thus reduced below the maximum in order to improve the notch toughness, the new titanium-boron steel still has an impressive advantage over other low-alloy ferritic steels in high-temperature rupture strength.

This is illustrated by Table III, where some of the room-temperature mechanical properties of the new titanium-boron steels, (listed in Table II) including notch-bar impact resistance, are given along with high-temperature test data.

TABLE III

Properties of titanium-boron steel after different heat treatments

Normalizing Temp., ° F	1,600	1,800	2,100	2,100	2,100
Tempering Temp., ° F	None	1,000	1,000	1,200	1,300
Av. Rockwell B. Hardness	40	46	92	85	73
Yield Strength, 0.2% Offset	31,000			70,300	
Tensile Strength, lbs. per sq. in	44,700			84,400	
Elongation in 2 in., per cent	44.0			21.0	
Reduction of Area, per cent	85.7			79.0	
Izod Impact Value, ft.-lbs	High	115	5-6	15-24	151
Hours for Rupture at 1100° F. and 30,000 lbs. per sq. in	Less than 1	Less than 1	490-496	119-240	Less than 1

If advantage is taken of the remarkable high temperature strength conferred by the combination of titanium and boron in low-carbon steel for service at over 1000° F., it may be desirable to add other alloys to the steel to improve its resistance to scaling, such as chromium up to 7%, silicon up to 3% or aluminum up to 2%, or combinations of these elements in smaller amounts.

These additions may very readily be made to the titanium-boron steel in the usual way, without interfering with the effect of the titanium-boron combination on the high-temperature strength.

In lieu of the titanium, other carbide formers such as columbium or zirconium may be included in the steel, as they function in the same fashion as titanium. Columbium has been found to act with boron in the same way as titanium when present in an effective amount. For instance the results given in Table IV, obtained on columbium steel at 1100° F., may be compared with those given in Table II for titanium steels, having been obtained from tests conducted in an identical manner.

TABLE IV

Time for rupture of columbium steels under constant stress at 1100° F.

Type of Steel	Heat Treatment, °F.		Stress, Lbs. per Sq. in.	Time for Rupture, Hours	Elongation, Per Cent in 2 in.
	Air-Cooled from—	Tempered, 1 hr. at—			
0.045% C, 0.66% Cb, no B	2100	1200	30,000	238	28.5
0.044% C, 0.78% Cb, 0.016% B	2100	1200	30,000	Over 401	

Although the steel in Table IV without boron compares favorably with those in Table II, it is evident that the columbium-boron combination gives definitely superior results.

What is claimed is:

1. An alloy of ferritic structure resistant to stress for extended periods at relatively high temperatures comprising 0.1 to 1% titanium, less than 0.1% carbon, and 0.01% to 0.10% boron, the remainder being essentially iron.

2. An alloy of ferritic structure resistant to stress for extended periods at relatively high temperatures comprising 0.01 to 0.1% carbon, 0.01 to 0.1% boron and titanium in an amount from 5 to 12 times the carbon content, the remainder being essentially iron.

3. An alloy of ferritic structure resistant to stress for extended periods at relatively high temperatures comprising 0.01 to 0.1% carbon, 0.01 to 0.1% boron and 0.1 to 2% of a carbide former selected from the class consisting of titanium, columbium and zirconium, the remainder being essentially iron.

4. An alloy of ferritic structure resistant to stress for extended periods at relatively high temperatures comprising 0.01 to 0.1% carbon, 0.01 to 0.1% boron and 0.1 to 2% of a carbide former selected from the class consisting of titanium, columbium and zirconium, up to 2% each of aluminum, manganese, nickel and copper, up to 3% silicon, and up to 7% chromium, the remainder being iron.

5. A steel of ferritic structure resistant to stress for extended periods at relatively high temperatures comprising 0.01 to 0.1% carbon, 0.01 to 0.1% boron, 0.1 to 2% of a carbide former selected from the class consisting of titanium, columbium and zirconium, 0.2 to 0.4% manganese, 0.01 to 0.1% silicon, 0.001 to 0.05% phosphorous, 0.001 to 0.05% sulfur, the remainder being iron.

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The following references are of record in the file of this patent:

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