

3,291,655
ALLOYS

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This invention relates to high temperature, high strength resistant ferritic steels which are characterized by improved creep-rupture ductility. More particularly, the invention relates to such alloys of the chromium-molybdenum-vanadium class which are characterized by good rupture ductility and high creep-rupture strength.

The use of Cr-Mo-V steels for high temperature, high stress service is well known. However, it has been found that when such steels are heat-treated at high austenitizing temperatures to increase the creep-rupture strength, the creep-rupture ductility tends to be lowered. It will be apparent that it is desirable not only to increase the creep-rupture strength of such steels, but to maintain the rupture ductility or resistance to embrittlement at optimum values. Where optimum creep-rupture strength is desired in Cr-Mo-V steels, complete solutioning of the vanadium carbides is required followed by cooling rapidly enough to allow the steel to transform to a predominantly bainitic microstructure followed by a tempering treatment usually in the temperature range of from about 1150° F. to 1400° F. to precipitate the vanadium in the form of vanadium carbide in a fine, uniformly dispersed phase. In this form, vanadium carbide is an efficient strengthener for high temperature creep and the finely dispersed vanadium carbides result in high hardness and creep-rupture strength, but at the same time a higher incidence of creep-rupture embrittlement. It has been common practice in the use of Cr-Mo-V steels, where creep-rupture ductility is important, to use a lower austenitizing temperature than that which is required for complete solution of the vanadium carbide. However, this reduces the creep-rupture strength appreciably and detracts from the use of the alloy in high temperature service where high stresses are encountered.

From the above it will be quite apparent that there is a need for Cr-Mo-V steels which can be heat-treated to achieve not only high rupture ductility but high creep-rupture strengths which will enable such alloys to resist high temperature stresses. Accordingly, a primary object of the invention is to achieve in high temperature Cr-Mo-V steels high rupture ductility and high creep-rupture strength at one and the same time.

Briefly, the invention relates to increasing the high temperature creep-rupture ductility at high creep-rupture strengths of cast and wrought ferritic steels of the Cr-Mo-V class by the addition to the molten alloy of aluminum and titanium. It has been found that in an alloy of the above class comprising by weight about 0.05 to 0.6% carbon, .5 to 3% chromium, 0.3 to 1.75% molybdenum, 0.15 to 1% vanadium, 0.2 to 1.5% manganese, with the remainder essentially iron, the rupture ductility of the alloy at high creep-rupture strengths is maintained by the addition to the molten alloy of such quantities of aluminum and titanium that at least about 0.02% aluminum and at least about 0.04% of titanium based on the weight of the molten alloy are present in the final alloy, the remainder of the aluminum and titanium added being in the combined state. Up to .2% residual aluminum and titanium have been found useful. The alloys of the invention are austenitized at such temperatures generally over 1800° F. that essentially all of the vanadium carbides are dissolved. The alloy is then cooled to allow

transformation to a predominantly bainitic structure and tempered as above.

The Cr-Mo-V steel alloys of the present invention are the result of a balance of ingredients or constituents which combine to provide the improved characteristics obtained. The carbon content of the alloy should be held to .05 to .6% if the optimum combination of high temperature characteristics is to be obtained. With carbon contents less or greater than those prescribed, it has been found that the high temperature creep-rupture strength of the steel is significantly lowered. Lower amounts of carbon within the above range are used where weldability is an important factor. The chromium content of the alloy is likewise quite critical and should be held to between .5 and about 3%. Additionally, a minimum of about .5% is required to provide resistance to graphitization. Commonly, from about .75 to 1.5% provides for oxidation resistance and this amount may be increased to about 3% when maximum oxidation resistance is desired. More than about 3% of chromium on the whole results in an undesirable reduction in creep-rupture strengths. The molybdenum content of the alloy should be maintained between about 0.3 to 1.75%. Less than about 0.3% molybdenum results in poor creep-rupture strength while more than about 1.75% molybdenum promotes the undesirable development of molybdenum carbides at the expense of vanadium carbide, again giving a lower creep-rupture strength. Vanadium in amounts of from about 0.15 to 1% results in improved creep-rupture strength. The prescribed manganese content of about 0.2 to 0.5% insures at its lower level that sulfur is in the form of manganese sulfide and larger amounts of manganese enhance the hardenability of the alloy. While amounts of manganese over about 1% lead to some slight decrease in creep-rupture strength, this is not significant in amounts up to about 1.5%.

Listed in Table I below are the percent by weight compositions of a number of alloys made in connection with the present invention. Shown in Table II are the room temperature, the tensile strength, yield strength, percent elongation and reduction in area under physical testing.

In Table I the percentages of aluminum and titanium in parentheses are those amounts added to the molten alloy, the other stated amounts of these metals being those present in the final alloy.

Alloys 1 through 21, 30 through 35 and 41 were prepared in an induction furnace. Alloys 22 through 24 and 36 through 38 were made in an electric furnace while alloys 26 through 29 were made in a plasma arc furnace. These varying modes of preparation account in part for the varying amounts of residual aluminum and titanium compared to the amounts added.

TABLE I

Alloy No.	C	Mn	Cr	Mo	V	Ti	Al
1	.17	.68	1.32	1.03	.59	.001	.038 (.02)
9	.22	.74	1.23	1.02	.71	<.01	1.010
10	.23	.77	1.28	1.00	.70	.074 (.15)	.011
11	.24	.82	1.31	1.00	.76	.074 (.15)	.031 (.03)
14	.24	.62	1.28	1.03	.75	.067	1.013
15	.24	.61	1.19	.97	.68	.063	1.018
17	.31	.74	1.26	1.12	.26	<.01	.042
18	.31	.52	1.10	1.10	.23	.091 (.15)	.008 (.03)
19	.30	.70	1.16	1.08	.28	.05	.035
20	.32	.75	1.17	1.08	.56	<.01	1.012
21	.31	.81	1.18	1.08	.60	.075 (.15)	.028 (.05)
22	.13	.76	1.30	1.00	.48	.063 (.10)	.027 (.03)
23	.17	.64	1.28	1.07	.46	.069 (.23)	.012 (.03)
24	.17	.68	1.35	1.00	.50	.040 (.17)	.014 (.03)
26	.14	.68	1.26	.97	.48	.003	1.005

TABLE I—Continued

Alloy No.	C	Mn	Cr	Mo	V	Ti	Al
27-----	.13	.69	1.28	.97	.49	.003	.017 (.008)
28-----	.13	.66	1.24	.97	.47	.003	.063 (.035)
29-----	.12	.66	1.25	.96	.46	.15 (.10)	.040 (.035)
30-----	.17	.64	1.32	.99	.58	.110 (.19)	1.009
31-----	.16	.66	1.32	.98	.56	.110 (.31)	.024 (.02)
32-----	.16	.64	1.30	.99	.57	.100 (.19)	.054 (.05)
33-----	.17	.63	1.34	.97	.57	.100 (.19)	.110 (.12)
34-----	.16	.67	1.35	.96	.60	.110 (.19)	.20 (.20)
35-----	.17	.64	1.35	1.00	.56	.12 (.21)	.013 (.01)
36-----	.22	.63	1.41	.98	.64	.037 (.09)	.025 (.025)
37-----	.21	.65	1.41	1.00	.64	.090 (.26)	.025 (.025)
38-----	.19	.65	1.40	1.00	.58	.088 (.26)	1.013
41-----	.16	.59	1.30	1.00	.57	.19 (.36)	.023 (.02)

¹ Residual aluminum—none added.

TABLE II

Alloy No.	Tensile Strength, p.s.i.	.2% Yield Strength, p.s.i.	Elongation, Percent	R.A., Percent
1-----	110,300	91,750	21.0	58.6
9-----	137,000	120,500	21.0	62.0
10-----	138,400	124,000	21.0	62.0
11-----	137,200	127,500	21.0	63.0
14-----	136,400	120,500	19.0	58.0
15-----	135,600	120,000	21.0	62.0
17-----	136,000	117,500	16.0	40.0
18-----	138,600	118,800	14.0	38.0
19-----	141,200	124,000	14.0	37.0
20-----	135,100	110,300	18.0	50.0
21-----	140,000	122,000	17.0	53.0
22-----	111,300	93,500	19.0	61.3
23-----	113,500	95,500	18.5	50.0
24-----	113,700	96,500	19.5	51.4
26-----	101,250	74,500	21.9	64.5
27-----	102,000	77,000	22.8	63.7
28-----	97,750		17.8	38.1
29-----	91,750	61,250	22.8	69.9
30-----	108,700	91,250	18.5	48.4
31-----	107,600	90,250	11.0	18.8
32-----	108,900	91,000	22.0	63.5
33-----	110,000	93,250	20.5	56.0
34-----	103,000	86,750	10.5	18.4
35-----	107,500	89,500	17.0	44.9
36-----	101,700	76,500	22.0	60.8
37-----	106,400	78,000	21.0	59.6
38-----	104,250	61,000	24.0	64.0
41-----	105,000	88,875	21.5	61.3

¹ 0.02% offset yield strength.

Alloys 1, 22 through 38 and 41 were cast while alloys 9 through 21 and 41 were forged. Alloy 1 was heat-treated for 16 hours at a temperature of 1875 to 1925° F., air-cooled, heat-treated for 15 hours at 1325° F. and air-cooled. The forged materials of alloys 9 through 15 were heat-treated at 1900° F. for 4 hours, air-cooled, and heat-treated at a temperature of 1300° F. for times ranging from about 6 hours to 8 hours. The forgings of alloys 17 through 21 were all heated for 4 hours at 1950° F., slow air-cooled over a period of 8 hours and reheated-treated for 20 hours at 1850° F. and again slow air-cooled over a period of 8 hours. Alloy 17 was additionally heated for 70 hours at 1200° F. as was alloy 19. Alloys 18 and 19 after the above heat treatment were again reheated at 1200° F. for 52 hours. Alloy 21 was further heat-treated at 1200° F. for 40 hours. Cast alloy 22 was heat-treated for 12 hours at 1922 to 1940° F., air-cooled and heated for 28 hours at 1319 to 1328° F. Cast alloy 23 was heat-treated for 14 hours at 1895 to 1940° F., air-cooled and further treated for 20 hours at 1301 to 1319° F. Alloy 24 was heat-treated for 20 hours at 1922 to 1931° F., air-cooled and further treated at 1310 to 1328° F. for 23 hours. Alloy 25 was heat-treated for 10 hours at 1875 to 1925° F., air-cooled and further treated at 75

1275 to 1325° F. for 20 hours. Alloys 26 through 29 were heat-treated for 12 hours at 1875 to 1925° F., air-cooled and heat-treated at 1300° F. for 25 hours. Alloys 30 through 35 were heat-treated for 15 hours at 1925° F., furnace-cooled, further heat-treated for 15 hours at 1364° F. and air-cooled. Alloys 36 through 38 were all initially heat-treated for 12 hours at 1950° F. and then furnace-cooled. Alloy 36 was further treated for 20 hours at 1350° F. and air-cooled, alloy 37 was further heat-treated at 1350° F. for 7 hours, while alloy 38 was further heat-treated at 1350° F. for 8 hours. Cast alloy 41 was heat-treated for 16 hours at 1875 to 1925° F., air-cooled, heat-treated at 1364° F. for 15 hours and air-cooled.

Shown in Table III below are the creep-rupture properties of the above alloys.

TABLE III—CREEP-RUPTURE PROPERTIES

Alloy No.	Temp., ° F.	Stress	Rupture Life, hours	Elongation, percent	R.A., percent
20	1,100	38,000	87.4	6.75	30
	1,100	34,000	292.3	3.35	12
	1,100	32,000	503.5	2.80	13
25	1,100	32,000	466.2	2.50	9.9
	1,100	60,000	12.0	10.0	52
	1,100	46,000	350.0	4.1	10
10	1,100	36,000	1,370.0	2.3	7.8
	1,200	25,000	566.0	9.7	19
	1,100	60,000	8.4	11.0	55
30	1,100	46,000	217.0	3.9	17
	1,100	34,000	1,237.0	2.9	14
	1,200	25,000	66.0	8.2	24
11	1,100	60,000	4.7	13.0	76
	1,100	46,000	246.0	13.0	58
	1,100	34,000	1,750.0	16.0	30
14	1,200	25,000	308.0	18.0	61
	1,100	60,000	75.0	4.4	8.5
	1,100	46,000	650.0	4.5	7.8
35	1,100	40,000	1,454.0	3.1	7.8
	1,200	25,000	956.0	5.0	27
	1,100	60,000	14.0	10.0	72
15	1,100	46,000	881.0	4.0	10
	1,100	42,000	1,103.0	4.4	23
	1,200	25,000	650.0	9.1	47
17	1,100	52,000	86.0	3.2	9.9
	1,100	46,000	170.0	3.7	8.5
	1,100	29,000	1,293.0	2.4	8.5
40	1,200	25,000	130.0	4.3	12
	1,100	52,000	72.0	9.4	34
	1,100	46,000	128.0	3.1	13
18	1,100	29,000	1,585.0	2.9	7.2
	1,200	25,000	141.0	8.4	26
	1,100	52,000	121.0	12.0	59
19	1,100	46,000	407.0	12.0	50
	1,100	34,000	1,584.0	6.6	39
	1,200	25,000	230.0	22.0	74
45	1,100	52,000	84.0	3.5	15
	1,100	46,000	312.0	5.2	17
	1,100	32,000	1,769.0	4.5	12
20	1,200	25,000	197.0	14.0	41
	1,100	52,000	74.0	16.0	77
	1,100	46,000	233.0	13.0	73
50	1,100	30,000	2,320.0	18.0	70
	1,200	25,000	152.0	14.0	81
	1,100	38,000	407.6	13.7	79
22	1,100	35,000	1,410.1	14.2	76
	1,100	38,000	3,332.4	14.7	76
	1,200	26,000	480.9	12.9	80
55	1,300	11,000	266.3	21.7	92
	1,100	38,500	804.6	9.3	60
	1,100	38,000	1,328.3	12.0	57
23	1,200	28,000	484.7	7.4	44
	1,300	14,000	417.2	13.2	73
	1,100	39,000	350.2	10.5	67
24	1,100	36,500	1,040.0	7.9	41
	1,100	36,000	1,387.2	8.1	38
	1,100	36,000	1,465.0	8.3	42
60	1,200	28,000	407.4	7.8	29
	1,300	13,000	408.4	10.5	54
	1,100	35,000	269.9	12.3	73
26	1,100	33,500	405.2	13.3	63
	1,100	32,000	649.7	13.3	55
	1,100	35,000	196.9	12.8	69
27	1,100	32,000	445.1	13.2	60
	1,100	30,000	1,132.9	9.0	44
	1,100	28,000	1,546.6	9.4	28
65	1,100	35,000	70.3	6.5	41
	1,100	32,000	407.7	12.9	59
	1,100	30,000	973.6	7.1	32
28	1,100	30,000	105.5	20.4	88
	1,100	27,000	504.3	20.3	83
	1,100	25,000	1,030.7	16.0	88
70	1,100	34.8	34.8	19.1	84
	1,100	35,000	128.8	23.0	86
	1,100	32,000	400.7	23.0	84
30	1,100	30,000	1,036.5	10.3	53
	1,100	38,000	33.2	25.8	83
	1,100	35,000	179.0	26.5	84
31	1,100	32,000	371.1	14.1	80
	1,100	30,000	845.1	15.1	67

TABLE III.—CREEP-RUPTURE PROPERTIES—Continued

Alloy No.	Temp., °F.	Stress	Rupture Life, hours	Elongation, percent	R.A., percent
32-----	1,100	38,000	36.7	23.7	83
	1,100	35,000	138.1	22.2	83
33-----	1,100	32,000	443.0	22.2	78
	1,100	38,000	96.3	22.8	82
34-----	1,100	32,000	972.0	14.5	71
	1,100	38,000	44.6	33.4	81
35-----	1,100	29,000	766.5	16.5	75
	1,100	35,000	168.2	17.6	81
36-----	1,100	32,000	297.7	11.9	56
	1,100	35,000	17.2	24.8	88
37-----	1,100	30,000	72.5	23.8	87
	1,100	23,000	1,314.3	20.9	41
38-----	1,100	35,000	45.0	21.3	86
	1,100	30,000	200.8	16.1	84
41-----	1,100	25,000	2,419.9	17.2	83
	1,100	38,000	7.5	14.9	79
41-----	1,100	34,000	57.1	15.5	79
	1,100	29,000	2,144.6	9.5	47
41-----	1,100	35,000	99.8	15.9	81
	1,100	32,000	293.0	15.8	83
	1,250	19,000	133.6	19.0	82

It will be seen from the above data that the addition to alloys of the type described of aluminum and titanium produces finished products which are not only characterized by high creep-rupture strength but at the same time are possessed of very desirable rupture ductility properties. It will be seen from a consideration of the data for alloy 1 wherein only aluminum is added to the alloy that the rupture ductility as evidenced by the percent reduction in area under stress at elevated temperatures leaves much to be desired in a cast product. Inspection of the data relating to Example 17 shows the same to be true of forgings to which only aluminum is added. Referring to cast alloy 38, it will be seen that the addition of titanium to the essential exclusion of or with only very small amounts of aluminum below the range prescribed produces an alloy which again has a decreasing rupture ductility at elevated temperatures. Alloy 18 illustrates the same effect for a forged material. Alloy 24 illustrates a cast material in which, while both aluminum and titanium are present, the relatively low amount of aluminum below the presently prescribed limits produces a material which is lacking in desirable rupture ductility. Alloy 14 illustrates this same effect of a deficient amount of aluminum for a forged product.

Alloy 27 is illustrative of a cast alloy in which, while a substantial amount of aluminum is present, there is a deficiency of titanium, once again, resulting in an undesirable rupture ductility. Alloy 28 shows that an increase in the amount of aluminum, still keeping the titanium at a low level, produces no pronounced improvement.

Alloy 15 (which contains 0.0016 boron for hardenability) illustrates a material having desirable rupture ductility by reason of its content of aluminum and titanium. Alloys 19, 22 and 34 are further illustrative of suitable materials according to the present invention.

Alloys 26, 27, 28 and 29 represent compositions which were obtained by making progressive additions of aluminum and finally 0.15% titanium to the same base heat of steel, castings being poured off after each addition. It will be noted that the rupture ductility progressively decreases through alloy 28 as the amount of aluminum is increased, showing that aluminum alone does not produce high rupture ductility. However, the addition of 0.15% titanium in alloy 29 results in a steel that shows no loss in creep-rupture ductility at all.

Alloys 9, 10, 11, 14 and 15 illustrate the effect of varying amounts of titanium and aluminum. Alloy 9 contains no deliberate additions of aluminum or titanium and shows low rupture ductility. Alloy 10 contains additional titanium but still shows no significant change in ductility. However, the addition of the aluminum indicated in alloys 11 and 15 produced, as will be seen, a significant increase in rupture ductility.

In a similar manner alloys 17, 18, 19 and 21 show the beneficial effect of titanium and aluminum additions

as in alloy 21 as compared to alloy 17 with aluminum alone or alloy 18 with titanium alone as pointed out above.

The alloys listed in Table I cover materials which are useful for many purposes. Alloys 17 through 21, for example, represent compositions which with the prescribed heat treatments are suitable for heavy forgings such as steam or turbine rotor forgings for high temperature service. Alloys 9 through 15 represent compositions and heat treatments suitable for smaller forgings and mill products such as plate and bar such as are used in pressure vessel construction for high temperature service. The remainder of the alloys represents compositions and heat treatments suitable for the production of castings, forgings or mill products for high temperature service where lower carbon contents are desirable for welding purposes.

It has been found that the order in which the aluminum and titanium are added is not critical and suitable steels have been made by adding either the aluminum or titanium first and also by adding both simultaneously. However, the recovery of the elements added is difficult to predict in some cases. However, it is believed that the most consistent melting practice results if the aluminum is added first or simultaneously with the titanium. It is also useful to combine the aluminum and titanium as a single pre-alloyed master alloy with suitable proportions of the critical ingredients indicated. The additions of aluminum and titanium should preferably be made after the oxidizing and refining proportion of the steelmaking practice and just prior to tapping if the additions are to be made in the furnace. The additions can also be made in the ladle during or after tapping and all of the above practices have been used with equal success.

It has been found that vacuum degassing produces in some partial degree the beneficial results obtained by adding the present materials so that with vacuum degassing lesser amounts of the additives are required. The present invention is intended to cover such practice.

There is provided then by the present invention means for realizing to the fullest extent the high creep-rupture strengths which are obtainable in Cr-Mo-V steels, at the same time providing such steels which have a desirably high rupture ductility.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A high temperature alloy characterized by high rupture ductility and high creep-rupture strength and having a bainitic structure with finely dispersed precipitated vanadium carbide, said alloy consisting essentially of by weight about .05 to .6% carbon, .5 to 3.0% chromium, 0.3 to 1.75% molybdenum, 0.15 to 1.0% vanadium, 0.2 to 1.5% manganese, from about .02 up to about 0.2% aluminum and from about 0.04 up to about 0.2% of titanium, with the remainder essentially iron.

2. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .24%, chromium 1.31%, molybdenum 1.00%, vanadium .76%, manganese .82%, aluminum .031%, and titanium .074%, with the remainder essentially iron.

3. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .30%, chromium 1.16%, molybdenum 1.08%, vanadium .28%, manganese .70%, aluminum .035%, and titanium .05%, with the remainder essentially iron.

4. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .31%, chromium 1.18%, molybdenum 1.08%, vanadium .60%, manganese .81%, aluminum .028%, and titanium .075%, with the remainder essentially iron.

5. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .13%, chromium 1.30%, molybdenum 1.00%, vanadium .48%, manganese .76%, aluminum .027%, and titanium .063%, with the remainder essentially iron.

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6. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .12%, chromium 1.25%, molybdenum .96%, vanadium .46%, manganese .66%, aluminum .040%, and titanium .15%, with the remainder essentially iron.

7. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .16%, chromium 1.32%, molybdenum .98%, vanadium .56%, manganese .66%, aluminum .024%, and titanium .110%, with the remainder essentially iron.

8. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .16%, chromium 1.30%, molybdenum .99%, vanadium .57%, manganese .64%, aluminum .054%, and titanium .100%, with the remainder essentially iron.

9. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .17%, chromium 1.34%, molybdenum .97%, vanadium .57%, manganese .63%, aluminum .110%, and titanium .100%, with the remainder essentially iron.

10. An alloy as in claim 1 wherein the constituents consist essentially of by weight carbon .21%, chromium 1.41%, molybdenum 1.00%, vanadium .64%, manganese

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.65%, aluminum .025%, and titanium .090%, with the remainder essentially iron.

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