United States Patent Office 3,433,626
Patented Mar. 18, 1969

3,433,626

METHOD OF ADDING OXYGEN TO TITANIUM AND TITANIUM ALLOYS

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No Drawing. Filed Feb. 1, 1966, Ser. No. 523,893
U.S. Cl. 75—10 9 Claims
Int. Cl. C22d 7/06; C22c 15/00

ABSTRACT OF THE DISCLOSURE

This invention relates to a method for strengthening reactive metals, such as titanium alloys, by the addition of interstitial strengthening additions, such as oxygen and nitrogen. In accordance with the invention, this is preferably achieved by adding to the reactive metal a metal oxide having a melting point below that of the reactive metal to which it is added.

Oxygen is commonly added to titanium base metals in the form of titanium dioxide, e.g., oxide scale or pellets comprising finely divided titanium dioxide and a suitable organic adhesive binder.

Titanium dioxide is a highly refractory compound with a melting point of approximately 1750° C. This is higher than the melting point of titanium and most titanium base alloys. For example, commercially pure titanium has a melting point of 1700° C. and the widely used Ti-6Al-4V alloy has a melting point of only 1600° C.

As a consequence of this difference in melting points, it becomes difficult or impossible in practice to obtain complete dissolution of added titanium dioxide, with the result that the final alloy contains mechanically disruptive defects, either in the form of undissolved titanium dioxide or localizations of high oxygen concentration having greatly decreased ductility. This is productive of localized internal defects—voids, cracks, etc., which are productive of failure of highly stressed parts made therefrom. Such internal defects can only be identified by a careful, expensive, and time-consuming examination, as by ultrasonic inspection. Therefore, such defects are known as "sonic defects."

Therefore, it is a primary object of the invention to provide an improved method of adding an interstitial strengthening element to titanium base metals and similar high melting point metals, such as zirconium, zirconium base alloys, and the like, which are commonly produced by the vacuum arc melting process.

It is another object of the invention to provide a new and improved method of adding oxygen to titanium base metals, zirconium, zirconium alloys and other high melting point metals.

It is a further object of the invention to provide a method of oxygen addition to titanium and titanium base alloys without the resultant production of sonic defects.

It is a still further object of the invention to provide a method of enhancing completeness and homogeneity of dissolution of oxygen additions to titanium base metals.

It is still another object of the invention to provide products of titanium base and similar metals having minimized sonic defects caused by incompletely dissolved and diffused oxygen.

In accordance with the foregoing objects, a preferred embodiment of the invention provides a method of adding oxygen to a vanadium-containing titanium base metal wherein oxygen is included, in the form of flakes or pellets of vanadium pentoxide, in compacted electrodes of titanium sponge and alloying elements.

These and other objects of the invention will become more readily apparent from an inspection of the following description.

A hard sonic defect was produced in an alloy comprising 5% aluminum, 2.5% tin, balance essentially titanium. This sonic defect was produced in the laboratory by placing scale in a small hole drilled in a 1 inch x 2 inch x 4 inch block of the alloy and then melting the metal in the defect area for one minute in a small vacuum arc furnace. After the melt cooled, sectioning of the block exposed the defect with its light and dark areas in the area of the void. The light area was found to have a diamond pyramid hardness (DPH) of 446 to 589 whereas the base metal hardness was 296 to 299 (DPH). The hard bright area was found to be caused by a localized high oxygen concentration as a result of nonuniform dissolution of the scale during melting. It is believed that the void resulted from subsequent shrinkage upon cooling because nonmetallic defects tend to have low cohesive strength and can nucleate a void under stress.

A hard sonic defect was found in an alloy comprising 6% aluminum, 4% vanadium, balance essentially titanium. A sample was examined on a plane normal to the rolling direction of the bar in which the defect was found. The hardness in the light areas adjacent to the void ranged from 413 to 453 DPH, and from 330 to 339 DPH in the matrix, indicating the defective material is quite brittle. The light areas were also found to contain more of the alpha phase of titanium than the matrix.

A hard sonic defect in an alloy comprising 6% aluminum, 4% vanadium, balance essentially titanium was found in a rolled billet of the alloy. Spectrographic analysis indicated there was no metallic difference between the defect and the matrix. The cracking found to be associated with the defect indicates this particular area was of low ductility. The hardness of the light area adjacent to the defect was found to be 660 DPH and that of the matrix 317 DPH.

On the basis of the foregoing studies demonstrating that TiO_2 additions (scale or pellets) could produce hard sonic defects, experimental melts using TiO_2 and V_2O_5 for oxygen additions were made.

Two 200-pound ingots were formulated to the same normal chemistry for a Ti-6Al-4V composition. Both charges were adjusted to the same oxygen level of 0.18% by using sponge analyzing 0.065% O_2 and by adding 0.115% oxygen in the form of TiO_2 (40% O_2) pills to one melt and V_2O_5 (44% O_2) pills to the other melt. Each pill used for both charges weighed ten grams. This required the addition of 0.030 pound of TiO_2 or 0.026 pound of V_2O_5 to the 40-pound briquette charges and a proportional amount to the 10-pound striker charges used for the first and second melts. After weighing, the individual charges were blended in the conventional manner with no noticeable breakup of the pills.

The 40-pound charges were then briquetted and assembled into two 200-pound consumable electrodes and consumably melted in a 12-inch mold at a pressure of approximately 10 microns, 5000 amperes, a reversing exciter current of 30 amperes, and with 10-pound striker charges. No difficulty was encountered during this first melt, and the surface quality of the ingots was comparable. The ingots were then remelted, without conditioning, into 15-inch molds at 10 microns pressure, 10,000 amperes, and the exciter coil set at 30 amperes, reversing, using 10-pound striker charges. Melting was done without problem, and again the ingot surfaces were similar and quite good.

The collars were removed from each ingot and the ingots were heated to 1800° F. for forging. Forging com-

menced, but was halted when surface cracks appeared on each ingot. The ingots were then cooled, partially conditioned by grinding, heated to 2050° F., upset and drawn out perpendicular to the central axis. One reheating to 2050° F. was required after upset and squaring but before draw-out. The billets were then finished to 8 inch x 8 inch cross-section, each showing several surface cracks from the initial forging operation.

Two-inch slices were sawed from the top, middle, and bottom of each billet for testing. The four remaining large pieces were ultrasonically tested for defects using a standard "Sperry reflectoscope" with a 2.25 megacycle, 1⅛"-round crystal, and a full screen scanning amplitude. Using a 3/64"-diameter hole as a checking amplitude, no sonic indications were found in the billet with the V_2O_5 addition; however, one indication of a hard sonic defect was found in the billet with the TiO_2 addition.

Chemical analysis of the billets was as shown in Table I, wherein the various elements are shown as being present in weight percent.

TABLE I.—CHEMICAL ANALYSIS OF 200-POUND MELTS

Steel No.	Oxide Addition	Ingot Location	Al	V	N	O
14509	TiO_2	Top	6.4	4.0	0.012	0.190
		Middle	6.3	4.0	0.015	0.188
		Bottom	6.4	4.0	0.016	0.196
		Average	6.4	4.0	0.014	0.191
		Deviation	0.1	0.0	0.004	0.008
14510	V_2O_5	Top	6.5	4.1	0.014	0.172
		Middle	6.4	4.1	0.017	0.180
		Bottom	6.5	4.1	0.012	0.176
		Average	6.5	4.1	0.014	0.176
		Deviation	0.1	0.0	0.005	0.008
Aim analysis			6.5	4.1	----------	0.180

From the foregoing table it can be seen that the chemistries of the two heats were quite uniform. Heat 14509 had a significantly higher oxygen content (+0.010%) than aimed for and heat 14510 was lower (−0.004%) than intended. A slight loss of V_2O_5 can be expected because of its higher vapor pressure. This, however, can be adjusted by adding an excess of V_2O_5 to the initial charge.

All sawed surfaces on the billets and test slices of the experimental heats were etched and examined for indications of hard sonics or other defects. Neither heat was found to contain hard sonics or gross oxide segregations at any of these locations. A surprising result of these macroetch tests was that the heat with the V_2O_5 addition showed a much finer grain size.

Specimens were prepared from the 2-inch slices from the billets for mechanical testing by upset hammer forging each section to 0.5 inch thick plate. Tensile test specimens were then prepared for testing each location in the annealed conditions. Results of these tests are summarized in Table II below.

TABLE II.—TENSILE TEST RESULTS OF 200-POUND MELTS

Heat No.	Location	Condition	Ultimate tensile strength (p.s.i.)	Yield strength at 0.2% offset (p.s.i.)	Elongation (percent)	Reduction of (percent)
14509	Top	Annealed [1]	142,500	128,700	12.0	30.9
	Middle	do [1]	144,300	129,600	12.0	24.2
	Bottom	do [1]	144,900	131,700	16.0	27.5
	Deviation	do [1]	2,400	3,000	4.0	6.7
14510	Top	Annealed [1]	143,300	133,800	16.0	38.9
	Middle	do [1]	143,000	134,700	16.0	43.8
	Bottom	do [1]	143,700	137,200	18.0	45.7
	Deviation	do [1]	600	1,500	2.0	6.8

[1] Specimens heated to 1,400° F. for one hour followed by air cool.

From Table II it can be seen that the annealed tensile properties for both heats were similar. Furthermore, it is evident that heat 14510 made with the V_2O_5 addition shows more uniformity of annealed properties from top to bottom of the ingot.

On the basis of the results obtained from the experimental melting a production heat of Ti-6Al-4V was scheduled for melting using V_2O_5 as an addition.

The electrode was formulated to a .13/.16 oxygen level in the conventional manner using sponge, master alloy, and V_2O_5 flake. V_2O_5 is commercially available in thin flake ranging in size from one-inch square down to dust. Commercial flake was screened using screens of 0.5 inch and 0.07 inch square openings. That portion of the flake passing through the 0.5 inch screen and remaining on the 0.07 inch screen was used to formulate the charge. The electrode was consumably melted yielding an ingot of approximately 9,000 pounds. Subsequent to solidification the ingot was reheated, forged to 10" x 12" square, and cut into six billets of equal length. The billets were identified AA, AB, BA, BB, XA, and XB respectively from top to bottom.

Test slices, 2" thick, were cut from either end of billet AA and the bottom of all other billets for chemical analysis. Results of these analyses are set forth in Table III below.

TABLE III.—CHEMICAL ANALYSIS OF BILLETS FROM 9,000-POUND MELT NO. G-14695

Billet	Location	Al			V			O		
		E	M	C	E	M	C	E	M	C
AA	Top	6.1	6.2	6.3	4.1	4.1	4.3	.160	.150	.140
	Bottom	6.4	6.3	6.3	4.0	4.1	4.1	.166	.155	.137
AB	do	6.1	6.1	6.1	4.1	4.0	4.0	.185	.166	.166
BA	do	6.2	6.3	6.3	4.0	4.0	3.9	.179	.173	.168
BB	do	6.1	6.3	6.1	4.0	4.0	4.0	.172	.174	.180
XA	do	6.2	6.3	6.3	4.0	4.2	4.2	.171	.170	.163
XB	do	6.2	6.3	6.1	4.0	4.1	4.0	.157	.147	.156
Ave		6.2	6.2	6.2	4.0	4.1	4.1	.170	.162	.159

E=Edge of disc; M=Midway of disc; C=Center of disc.

From the foregoing table it is evident that the alloy distribution was very good and oxygen distribution was satisfactory. The lower oxygen in the edge and midway portions of the top and bottom of Billet AA are believed to be normal for titanium ingots due to freezing segregation at the extreme top of the ingot. This has been found on other melts of this Ti-6-Al-4V grade when TiO_2 instead of V_2O_5 was used as an addition.

Tensile specimens were prepared from the slices taken

from the bottoms of billets AA and XA. Results of the tensile tests are set forth in Table IV.

TABLE IV.—TENSILE TEST RESULTS 9,000-POUND HEAT

Billet	Condition	Ultimate strength (p.s.i.)	Yield strength at 0.2% offset (p.s.i.)	Elongation (percent)	Reduction of area (percent)
AA	Annealed [1]	160,625	154,550	12.8	43.2
		159,625	155,250	15.0	42.6
XA	do [1]	163,450	159,475	13.4	44.6
		160,900	155,800	14.0	43.0
AA	Heat treated [2]	177,900	168,025	12.4	46.4
		176,675	166,425	14.0	50.5
XA	do [3]	173,725	167,275	12.2	53.1
		175,250	166,700	13.0	53.5
Aim	do [2]	[3] 170,000	[3] 160,000	[3] 8.0	

[1] Heat 1,300° F. for 2¼ hours, furnace cool 5°/minute to 1,000° F., air cool.
[2] Heat 1,750° F. for 1½ hours, water quench, age 1,000° F. 8 hours.
[3] Minimum.

From Table IV it can be seen that the ingot showed fairly uniform tensile properties from top to bottom in both the annealed and heat treated conditions.

The billets were subsequently rolled to 3¼ inch square billets, ground on four sides, and sonic tested by both water immersion and contact methods. Neither sonic test method revealed any indication of hard sonic type defects.

Macroetch tests taken from either end of the 3¼ inch square billets did not reveal any indication of hard sonic defects or gross oxide segregations.

The V_2O_5 is preferably added in the form of flake or pills rather than powder, to prevent stratification of the addition in the charge. When the pills or flake are blended in the charge and compacted into the electrode, they are uniformly dispersed throughout. Powder, on the other hand, tends to sift down through the charge and collect in a layer at the bottom of the compact.

It is evident that other nonrefractory oxides, i.e., oxides having a melting point lower than the base metal, would be useful in adding oxygen to titanium base alloys or other refractory metals or alloys containing the metallic constituent of the oxide as an alloying element. A partial list of such oxide compounds, useful for adding oxygen to titanium base metals, is set forth in Table V along with the melting points of such compounds (that of Ti being, as aforesaid, about 1700° C.).

TABLE V.—USEFUL OXIDE COMPOUNDS FOR ALLOYING AND ADDING OXYGEN TO TITANIUM BASE METALS

Compound:	Melting point (° C.)
SnO_2	1127
FeO	1420
Fe_2O_3	[1] 1560
Fe_3O_4	[1] 1538
Cu_2O	1235
MnO	1650
MoO_3	795
Bi_2O_3	840
Cb_2O_3	1460
SiO_2	1715
V_2O_5	800

[1] Compound decomposes.

The metallic elements of the compounds set forth in Table V are well-known alloying constituents of titanium. SiO_2 melts above the melting point of pure titanium; however, the difference (+15° C.) would not prevent use of this compound.

Metallic oxide compounds having a melting point below that of the base metal and wherein the metallic element neither forms a desirable alloy with or imparts deleterious properties to the final alloy may also be used to introduce oxygen into titanium base alloys.

There has been some consideration given to producing interstitially strengthened titanium and titanium base alloys by adding nitrogen to the metal. Using the technique of the instant invention, this can be accomplished by using compounds such as chromium nitride (CrN, melting point 1770° C.) wherein an alloy of chromium and titanium is desired to be intersitially strengthened.

While I have shown and described a single embodiment of the invention, I intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

I claim:

1. A method of introducing an interstitial strengthening element into a metal alloy comprising a base metal and a minor portion of at least one alloying element, wherein the interstitial strengthening element is soluble in the base metal, which comprises adding to a particulate mixture of the base metal, and alloying elements, a compound of the alloying element and interstitial strengthening element, which compound has a melting point below that of the base metal, and vacuum arc melting the resulting admixture.

2. A method in accordance with claim 1, wherein the compound is added in pellet form.

3. A method in accordance with claim 1, wherein the compound is added in flake form.

4. A method in accordance with claim 3, wherein the flakes have a mean maximum dimension greater than 0.07 inch.

5. A method in accordance with claim 1, wherein the base metal is titanium.

6. A method in accordance with claim 5, wherein the interstitial strengthening element is oxygen.

7. A method in accordance with claim 6, wherein the compound is vanadium pentoxide.

8. A method of introducing an interstitial strengthening element selected from the group consisting of oxygen and nitrogen into a metal alloy comprising a base element selected from the group consisting of titanium and zirconium and a minor portion of an alloying element selected from the group consisting of vanadium, molybdenum, tin, iron, copper, manganese, bismuth, columbium, silicon and mixtures thereof, which comprises adding to a particulate mixture of the base and alloying elements a compound of the alloying element and interstitial strentghening element having a melting point below that of the base metal, and vacuum arc melting the resulting admixture.

9. A method of introducing an interstitial strengthening element selected from the group consisting of oxygen and nitrogen into a vacuum arc melting metal alloy comprising a base element selected from the group consisting of titanium and zirconium and a minor portion of an alloying element selected from the group consisting of vanadium, molybdenum, tin, iron, copper, manganese, bismuth, columbium, silicon, and mixtures thereof, which comprises adding to a particulate mixture of the base and alloying elements a compound of the alloying element and interstitial strengthening element having a melt-

ing point below that of the base metal, forming the mixture into an electrode, and vacuum arc melting the electrode.

References Cited

UNITED STATES PATENTS

2,797,996	7/1957	Jaffee et al.	75—175.5
3,005,246	10/1961	Murphy et al.	75—10 XR
3,028,234	4/1962	Alexander et al.	75—175.5 XR
3,258,335	6/1966	Hatch	75—175.5

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U.S. Cl. X.R.

75—175.5, 177