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3,485,683

**METHOD OF HEAT TREATING A DUCTILE
AUSTENITIC DUCTILE IRON CASTING IN-
CLUDING REFRIGERATION TREATMENT
AND ARTICLE PRODUCED THEREBY**

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No Drawing. Filed Dec. 15, 1966, Ser. No. 601,844
Int. Cl. C21d 1/26; C22c 41/02, 41/04
U.S. Cl. 148—125

9 Claims 10

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ABSTRACT OF THE DISCLOSURE

Directed to austenitic ductile irons containing about 15% to about 26% nickel and at least one other element, such as 0.6% to 1.3% chromium, 0.4% to about 1.5% molybdenum, and 0.4% to about 2% tungsten, which respond to a thermal treatment comprising a heating at about 1700° F., a slow cool, a refrigeration at about -100° F., and a re-austenitizing treatment to provide high strength ductility and corrosion resistance in the castings.

The present invention relates to austenitic cast iron products having improved strength and ductility, and to special methods for producing such products.

The desirable properties of austenitic cast irons having either flake graphite structures or spheroidal graphite structures have long been known in the art. These materials afford a means for providing complex parts of many types, for example, pump housings, turbine housings, etc., by the relatively inexpensive casting process while at the same time providing final articles having excellent corrosion resistance in certain media, having useful strength levels, etc.

It has been recognized that it would be a commercially desirable objective to provide in austenitic cast irons an even higher level of strength, e.g., 45,000 pounds per square inch (p.s.i.) yield strength (0.2% offset) than that presently obtainable in such castings, i.e., a yield strength of about 35,000 p.s.i., while at the same time retaining the highly desirable ductility and corrosion resistance which characterize the materials. We have now discovered a particularly advantageous means for providing in austenitic cast irons improved strength and ductility properties as compared to the properties available in the materials in the as-cast condition, and have discovered special austenitic cast iron compositions which are particularly amenable to the special processing contemplated in accordance with the invention.

It is an object of the present invention to provide a method for improving the strength of austenitic cast iron castings.

It is a further object of the invention to provide a method for improving the mechanical properties of austenitic ductile irons which is relatively inexpensive and which may be carried out by readily available commercial means.

It is another object of the invention to provide special austenitic ductile iron compositions which are particularly amenable to improvement by the methods contemplated in accordance with the invention.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention is directed to the treatment of austenitic ductile iron compositions containing, by weight, about 15% to about 26% nickel, about 1.5% to about 3.5% carbon, up to about 4.5% or about 6% silicon, up to about 1% or about 1.5% manganese, at least one element from the group consisting of chromium, molybdenum and tungsten related such that the sum of percent chromium plus 0.7 times percent molybdenum plus 0.5 times percent tungsten is at least about 0.2 to about 2.5, magnesium in an effective amount up to about 0.15% to spheroidize graphite in the castings, with the balance except for minor amounts of elements not materially effective in changing the basic and novel characteristics of the alloys being essentially iron, to a thermal treatment comprising heating at about 1600° F. to about 1800° F. for about one to about four hours, e.g., about 1700° F. for about two hours, followed by cooling to about room temperature, refrigeration to a temperature of about minus 50° F. or about minus 80° F. to about minus 120° F. or about minus 150° F., e.g., minus 109° F., for at least one hour to about four hours, e.g., about two hours, to produce a martensitic structure, and a final heating (re-austenitizing) to a temperature in the range of about 1100° F. to about 1400° F. or about 1500° F. or even 1600° F., and air cooling. The composition of the iron treated and the temperature employed in the refrigeration step in degrees Fahrenheit are correlated such that the relationship 50 times percent Mn plus 24 times percent Ni plus 60 times percent Cr plus 19 times percent W minus 20 times percent Si plus 20 times percent Cu plus 21 times percent Mo plus refrigeration temperature in degrees Fahrenheit is equal to a factor between 306 and 506.

In the alloys contemplated in accordance with the invention, carbon and nickel are always present and, generally, in the interest of castability and for control of carbon equivalent, silicon is also present. Accordingly, the elements chromium, tungsten, copper and molybdenum, which are optionally present, must be carefully weighted against nickel and silicon and refrigeration temperature in accordance with the aforementioned relationship. Carbon is present in the castings in amounts of at least 1.5% and up to about 3.5%. Thus, when carbon is present in lesser amounts than 1.5%, castability is detrimentally affected and there is an undesirable increased tendency for carbide formation during solidification of the castings. Excessive carbide formation in the alloys is undesirable from the ductility standpoint. On the other hand, as carbon is increased beyond about 3.5%, there is an increased tendency for graphite flotation from the melt, for the formation of vermicular graphite, and of reductions in strength and elongation. Silicon also affects the casting characteristics through its effect upon carbon equivalent. Silicon may be present in amounts up to about 6% since it contributes to martensite formation during the refrigeration, helps prevent undesirable carbide formation, and inhibits loss of strength during the re-austenitizing heat treatment. Silicon present in amounts of at least about 2.5% or 3% also contributes importantly to hardening and strength in the castings. On the other hand, silicon desirably does not exceed about 6%, or, more advantageously, about 4.5%, as otherwise there is

an undesirably increased formation of ferrite in the castings with accompanying reduction in ductility. Nickel is an essential element in the castings, particularly from the standpoints of corrosion resistance and desired microstructural control, including inhibition of carbide formation, and is present in amounts of at least about 15% to provide austenite in the as-cast condition in the alloy but does not exceed about 26% as otherwise there is a reduced tendency to the formation of martensite during refrigeration at temperatures not lower than about minus 100° F. Advantageously, the nickel content is about 18% to about 22%. Chromium, molybdenum and tungsten are essential strengthening and hardening elements, either singly or in combination, and may be present in amounts up to about 2.5%, up to 3.5% and up to about 5%, respectively. All of these elements are strong carbide formers, served to lower Ms temperature, and permit reaustenitization of castings without excessive loss of hardness and strength. These elements also permit extension of the reheat temperature range while retaining useful combinations of properties. The elements are advantageously employed in amounts of about 0.6% to about 1.3% chromium, about 0.4% to about 1.5% molybdenum, and about 0.4% to about 2% tungsten, and are governed by the proportioning equation, also set forth hereinbefore. Such advantageous alloys, i.e., alloys containing about 18% to 22% nickel and an advantageous amount of chromium, molybdenum and/or tungsten, are characterized by yield strengths (0.2% offset) in the properly reaustenitized condition of at least about 45,000 p.s.i. along with tensile elongations of at least about 10%. Tungsten and molybdenum promote retention of yield strength in the reaustenitized castings upon exposure of cast specimens made of alloys containing these elements to service temperatures on the order of up to about 1100° F. Manganese is included in limited amounts not exceeding about 1.5% in the castings. Manganese is a mild carbide former during solidification and inhibits the formation of martensite in the castings. Excessive manganese contents cause pinholing in the castings and nickel-manganese alloyed irons are insufficiently hardenable at alloy levels which retain the required corrosion resistance. Copper may be included in the austenitic ductile iron castings contemplated in accordance with the invention in amounts up to about 3% or about 4% provided an addition of a rare earth metal such as cerium is also employed to overcome the interference of copper upon the graphite-spheroidizing effect of magnesium.

It is to be understood that the stepwise treatment accomplished in accordance with the invention comprises first a high temperature anneal which, in most cases, is necessary as an initial conditioning treatment to provide an austenite to martensite conversion during the subsequent refrigerating step. Cooling from the anneal is conducted at a slow rate, e.g., a rate comparable to a furnace cool, in order to avoid distortion of castings and other undesirable physical effects, and in order to enhance the effectiveness of the subsequent refrigeration treatment. In the refrigeration step, it is most advantageous from the standpoint of convenience and cost that the temperature necessary to produce a substantial amount of martensite upon refrigeration not be substantially below minus 110° F., e.g., minus 100° F. to about minus 120° F. The special relationship of alloying elements and refrigerating temperature set forth hereinbefore generally insures that satisfactory martensite conversion will be achieved at refrigerating temperatures not substantially lower than about minus 110° F. The ability to employ a refrigerating temperature on the order of minus 109° F. enables the use of inexpensive refrigerating techniques such as dry ice or readily available mechanical refrigerating equipment. It is quite important from the cost standpoint to realize substantial conversion of austenite to martensite during the refrigeration step without the necessity of employing excessively low temperatures, e.g.,

minus 320° F. The final heating step which is usually conducted in the temperature range of about 1100° F. to about 1400° F. or higher in some cases serves to reaustenitize the martensitic structure achieved during refrigeration. It is usually sufficient to conduct the reheating for the time required to bring the casting to temperature. This time is considered to be about one hour for each inch of casting thickness. Cooling from the final heating step can again be at any convenient rate but most desirably is an air cool. It is found that the heat treatment accomplished in accordance with the invention not only substantially raises the yield strength of the austenitic ductile iron castings but also retains the tensile elongation thereof. Thus, the yield strength of an austenitic ductile iron composition containing about 2.63% carbon, 3.65% silicon, 19.8% nickel, 0.66% manganese, 1.02% chromium, 0.092% magnesium and the balance essentially iron was increased from about 30,000 p.s.i. in the as-cast state to 50,200 p.s.i. while maintaining approximately the same elongation by means of treatment in accordance with the invention involving a heating at 1700° F. for two hours, furnace cool, refrigeration at minus 100° F. for two hours, and a reheating at 1400° F. for two hours plus air cool.

In order to give those skilled in the art a better appreciation of the advantages of the invention, a number of austenitic ductile iron castings were produced by induction melting charges of pig iron, commercially pure ingot iron, ferroalloys, electrolytic nickel and chromium, superheating the melts to about 2850° F., treating the melts with a nickel-magnesium alloy containing about 15% magnesium at a melt temperature of about 2750° F., inoculating the treated melts with a ferrosilicon alloy containing about 85% silicon and casting the inoculated melts into molds to provide castings having compositions as set forth in the following Table I:

TABLE I

Alloy No.	Percent						
	C	Si	Ni	Mn	Cr	Mg	Others
1.....	2.71	2.04	19.1	0.74	0.32	0.06	
2.....	2.68	1.89	19.4	0.74	0.63	0.063	
3.....	2.65	1.87	19.3	0.77	0.94	0.067	
4.....	2.85	1.65	19.3	0.66	1.05	0.053	
5.....	2.82	2.35	19.5	0.66	1.05	0.060	
6.....	2.62	2.95	19.8	0.66	1.02	0.086	
7.....	2.63	3.65	19.8	0.66	1.02	0.092	
8.....	3.06	1.45	21.1	0.69	-----	0.066	0.28 W
9.....	3.06	1.75	21.1	0.69	-----	0.11	0.51 W
10.....	2.93	1.43	21.05	0.66	-----	0.07	2.0 W
11.....	2.99	1.52	21.05	0.66	-----	0.094	4.5 W
12.....	2.62	2.21	19.2	0.85	-----	0.073	0.99 Mo
13.....	2.57	2.42	19.5	0.80	-----	0.078	1.48 Mo
14.....	2.83	3.50	20.0	0.29	0.88	0.062	
15.....	2.82	3.40	20.0	0.99	0.98	0.063	
16.....	2.70	1.65	15.7	1.0	2.2	0.058	

Castings made from these alloys were subjected to an anneal at 1700° F. for two hours followed by furnace cooling and were refrigerated in a dry ice-alcohol bath at minus 109° F. for two hours. Thereafter, the refrigerated castings were reheated at various temperatures within the range of 1100° F. to 1500° F. for about two hours. The hardness of the castings after refrigeration and after reheating are set forth in the following Table II, together with the mechanical properties after the reaustenitizing heat treatment:

TABLE II

Alloy No.	Refrigerated, BHN	Reheat temp., °F.	Reaustenitized Mechanical Properties				
			BHN	YS, 0.2% offset, p.s.i.	T.S., p.s.i.	Percent	
						EL,	R.A.
1.....	387	1,200	198	44,500	102,000	11.0	8.0
		1,300	158	28,000	95,000	16.0	14.0
2.....	368	1,200	203	49,900	106,300	13.7	12.5
		1,300	182	44,900	99,400	18.5	16.0
3.....	340	1,200	200	50,200	99,700	13.5	11.0
		1,300	190	46,700	93,100	17.5	15.5

TABLE II—Continued

Alloy No.	Refrigerated, BHN	Reheat temp., ° F.	Reaustenitized Mechanical Properties				
			BHN	Y.S., 0.2% offset, p.s.i.	T.S., p.s.i.	Percent	
						El.	R. A.
4	287	1,200	173	45,100	93,900	14.5	14.0
		1,300	167	43,500	87,300	17.0	16.5
5	321	1,200	183	49,700	100,200	14.5	13.0
		1,300	170	48,000	90,000	17.0	13.5
6	344	1,200	205	48,400	108,700	17.5	13.0
		1,300	199	52,700	104,900	20.5	16.5
		1,400	163	44,900	90,600	27.0	23.5
7	351	1,200	211	51,900	96,000	11.5	10.0
		1,300	196	54,200	99,900	16.5	11.0
		1,400	182	50,200	97,000	25.0	20.5
8	327	1,150	180	48,700	94,100	22.5	18.7
		1,250	170	39,900	97,300	19.5	17.0
		1,350	160	34,000	92,600	21.5	18.5
9	302	1,150	182	49,400	88,400	19.0	14.5
		1,250	176	46,700	87,000	14.5	11.5
		1,350	170	44,400	90,200	20.0	17.0
10	255	1,150	182	50,200	89,900	16.5	14.0
		1,250	170	46,600	91,400	16.5	14.0
		1,350	173	44,600	87,700	19.0	14.5
11	192	1,150	194	46,500	79,400	11.0	12.0
		1,250	182	43,800	79,700	11.5	9.5
		1,350	170	42,800	78,200	11.5	12.5
12	397	1,400	216	44,900	49,600	11.5	12.5
13	364	1,400	218	41,100	47,400	9.0	15.0
14	393	1,500	207	39,600	46,600	6.5	11.0
		1,300	199	45,800	117,300	15.0	13.0
15	317	1,400	156	33,800	101,500	27.0	23.0
		1,300	185	50,000	95,800	24.5	18.5
16	277	1,400	170	44,200	85,300	35.5	24.0
		1,100	255	59,200	90,600	4.5	3.0
		1,200	216	49,800	81,000	6.0	4.5
		1,300	217	50,200	79,400	6.5	6.0
		1,400	207	48,900	64,800	4.5	6.0

NOTE.—Tensile properties given for Alloys Nos. 12 and 13 represent the average of two determinations at 1100° F. testing temperature.

BHN=Brinell Hardness Number.

Y.S.=Yield strength.

T.S.=Tensile strength.

El.=Elongation.

R.A.=Reduction in area.

Rupture testing of Alloys Nos. 12 and 13 at 1100° F. indicated a 1000-hour rupture strength of 21,000 p.s.i. and 22,500 p.s.i., respectively.

Alloys provided in accordance with the invention are useful in many applications in which corrosion resistance, strength, ductility and/or elevated temperature strength in a cast material are required. Thus, alloys such as Alloy No. 7 are useful in shipboard fittings. Castings made of alloys Nos. 8 through 13 are characterized by stable carbides and are useful for elevated temperature service in applications such as turbine casings and housings. Alloys such as Alloy No. 16 are useful in applications such as pump bodies and impellers, valves and pipe joints and in other applications in which corrosion-erosion resistance and strength are required. This alloy when treated in accordance with the invention has a structure comprising carbides dispersed in austenite. The properties of Alloys Nos. 1 through 3 demonstrate that increasing chromium from about 0.3% to about 1% increases strength in the alloys while the properties of Alloys Nos. 4 through 7 demonstrate that silicon exhibits a marked strengthening effect. The data demonstrate that proper alloying permits broadening the range of reheat temperatures while still retaining useful combinations of strength and ductility in the castings. Alloys Nos. 12 and 13, in particular, displayed market resistance to softening when reaustenitized at 1400° F. The high elongation and reduction in area results given in Table II indicate the high toughness of these materials.

In contrast to the outstanding combinations of properties which characterize castings made of the special austenitic ductile iron compositions treated in accordance with the invention, it can be pointed out that the standard Type D-2 austenitic ductile iron specified in A.S.T.M. Designation A 439-62 is characterized, in the as-cast condition, by a yield strength (0.2% offset) of 32,000 to 36,000 p.s.i., a tensile strength of 55,000 to 69,000 p.s.i., and an elongation of 8% to 20%.

In addition to the applications mentioned hereinbefore,

cast alloy articles provided in accordance with the invention are useful in diesel engine cylinder liners, pump casings and other parts and in other castings in which resistance to corrosion and erosion are required. The improved strength which characterizes the alloys makes possible the use of lighter sections, thereby saving weight.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. The method for producing austenitic ductile iron castings having improved strength which comprises subjecting a casting containing, by weight, about 15% to about 26% nickel, about 1.5% to about 3.5% carbon, silicon present in amounts up to about 6%, up to about 4% copper, up to about 1.5% manganese, at least one element from the group consisting of up to about 2.5% chromium, up to about 3.5% molybdenum and up to about 5% tungsten related such that the sum of chromium plus 0.7 times molybdenum plus 0.5 times tungsten is about 0.2 to about 2.5, a small amount of magnesium up to about 0.15% effective to spheroidize graphite in the casting, an amount of rare earth metal effective to overcome the deleterious effect of copper present upon the spheroidal graphite structure and the balance essentially iron to a treatment comprising a heating at about 1600° F. to about 1800° F. for about one to about four hours, a slow cool at a rate equivalent to a furnace cool, a refrigeration treatment in the range of about minus 50° F. to about minus 150° F. for at least about one hour to produce martensite in said casting and a reaustenitizing treatment at a temperature of at least about 1100° F. up to about 1600° F., with the composition of said casting and the refrigeration temperature being controlled such that the quantity 50 times percent Mn plus 24 times percent Ni plus 60 times percent Cr plus 19 times percent W minus 20 times percent Si plus 20 times percent Cu plus 21 times percent Mo plus refrigeration temperature in degrees Fahrenheit is equal to a factor between 306 and 506.

2. The method according to claim 1 wherein the heating step is conducted at about 1700° F. for about two hours.

3. The method according to claim 1 wherein the refrigeration step is conducted at a temperature between minus 80° F. and minus 120° F.

4. The method according to claim 1 wherein the refrigeration step is conducted in Dry Ice.

5. The method according to claim 1 wherein the reaustenitizing step is conducted in the temperature range of about 1100° F. to about 1400° F.

6. The method according to claim 1 wherein the alloy composition employed contains at least one element from the group consisting of about 0.6% to about 1.3% chromium, about 0.4% to about 1.5% molybdenum and about 0.4% to about 2% tungsten.

7. The method according to claim 6 wherein the alloy contains about 18% to about 22% nickel.

8. The method according to claim 6 wherein the alloy contains about 2.5% to about 4.5% silicon.

9. An austenitic ductile iron casting characterized by improved strength and having a structure resulting from a thermal treatment comprising a heating at about 1700° F. followed by a slow cool at a rate equivalent to a furnace cool, a refrigeration at about minus 50° F. to about minus 150° F. and a reaustenitizing treatment at a temperature of at least about 1100° F. to about 1600° F. comprising, by weight, about 18% to about 22% nickel, about 1.5% to about 3.5% carbon, about 2.5% to about 4.5% silicon, up to about 1.5% manganese, at 0.6% to about 1.3% chromium, about 0.4% to about

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least one element from the group consisting of about 1.5% molybdenum and about 0.4% to about 1.5% tungsten, with the sum of chromium, 0.7 times molybdenum and 0.5 times tungsten not exceeding about 2.5, a small amount of magnesium effective to spheroidize graphite in said casting, with the casting composition being further related such that the sum of 50 times percent manganese, 24 times percent nickel, 60 times percent chromium, 19 times percent tungsten, 21 times percent molybdenum minus 20 times percent silicon, minus 109 is equal to a factor between 306 and 506, and with the balance being essentially iron.

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HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

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UNITED STATES PATENTS

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,485,683 Dated Dec. 23, 1969

Inventor(s) Robert D. Schelleng and Frederick K. Kies

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 6, line 75 (line 11 of claim 9) should appear as Col. 7, line 1 (line 12 of claim 9) and Col. 7, line 1 (line 12 of claim 9) should appear as Col. 6, line 75 (line 11 of claim 9)

Signed and sealed this 29th day of June 1971.

(SEAL)
Attest:

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