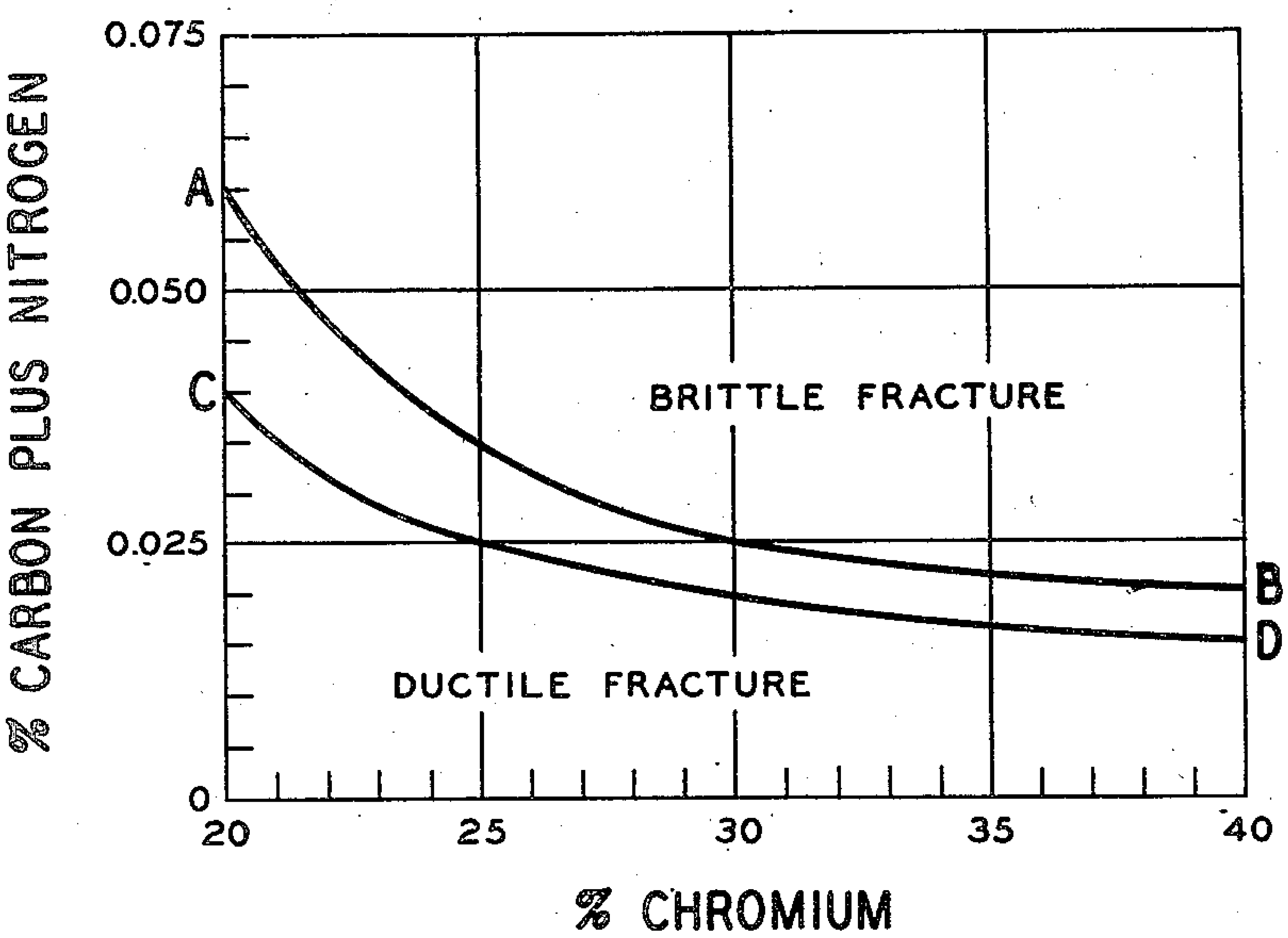
Jan. 6, 1953 W. O. BINDER ET AL 2,624,671
FERRITIC CHROMIUM STEELS
Filed Jan. 19, 1951



INVENTORS
WILLIAM O. BINDER
RUSSELL FRANKS
BY D.C. Harrison
ATTORNEY

Patented Jan. 6, 1953

2,624,671

UNITED STATES PATENT OFFICE

2,624,671

FERRITIC CHROMIUM STEELS

William O. Binder, Niagara Falls, N. Y., and Russell Franks, Pittsburgh, Pa., assignors to Union Carbide and Carbon Corporation, a corporation of New York

Application January 19, 1951, Serial No. 206,906

6 Claims. (Cl. 75—126)

1

This invention relates to ferritic chromium steels suitable for the fabrication of equipment required to possess good toughness and ductility in addition to resistance to corrosion and oxidation.

The so-called "straight" ferritic chromium steels have found limited utility in the past because as chromium is increased to provide necessary resistance to oxidation and other corrosion, the toughness of the steels at ordinary room temperatures decreases sharply. Thus, although steels containing more than 20% chromium are excellent from the standpoint of corrosion and oxidation-resistance, they are notch sensitive, and for applications where toughness is required, of the ferritic chromium steels only those containing not more than 20% chromium could be used, and generally the chromium content has not exceeded 16%. The notch sensitivity developed by ferritic steels containing more than 20% chromium has engaged the attention of metallurgists for many years, but no satisfactory solution to the problem, whether heat treatment or modification of composition, has been achieved.

It is the principal object of this invention to provide ferritic chromium steels containing 20% to 40% chromium which steels are tough and ductile at ordinary room temperatures and lower temperatures. More specifically, it is an object of the invention to provide ferritic steels containing 20% to 40% chromium which have an Izod impact strength of at least 18 foot pounds at room temperature. Another object is the provision of articles fabricated from such steels, which articles in normal use are required to possess good resistance to corrosion and oxidation and to retain toughness and ductility.

The invention by means of which these objects are attained is based upon the discovery that there is a critical relationship in ferritic chromium steels containing 20% to 40% chromium between the toughness of such steels and the sum of their carbon and nitrogen contents. Further, it has been found that as chromium is increased from 20% to 40% the tolerance for carbon and nitrogen to retain toughness decreases and that the relationship between chrominum and the sum of carbon and nitrogen may be represented by a curve which separates steels which retain toughness at room temperature and below from steels which are brittle at room temperature.

The single figure of the drawing is a pair of curves, AB and CD, representing the critical relationship between chromium and the sum of carbon and nitrogen in ferritic chromium steels containing 20% to 40% chromium.

2

The invention comprises ferritic chromium steels containing 20% to 40% chromium, carbon and nitrogen in such proportions that their sum for any selected chromium content when plotted against the chromium content as in the drawing does not fall above the curve, AB, and is preferably below the curve CD, the remainder essentially iron and the customary additions and impurities ordinarily present in steels of this type. As is illustrated by the drawing, a steel containing 20% chromium may contain carbon and nitrogen in a sum not above about 0.06% and be ductile, but a steel containing 25% chromium must contain not more than 0.035% carbon and nitrogen to be free of brittleness at room temperature, while at 40% chromium the sum of carbon and nitrogen must be less than about 0.02%. For applications where it is important to have greatest impact strength, it is preferred that the composition of a steel to be used fall below the curve, CD. Representative upper limits for the sum of carbon and nitrogen under these conditions are 0.04% at 20% chromium; 0.025% at 25% chromium and 0.015% at 40% chromium.

The explanation for the rapid decrease in toughness of commercial ferritic chromium steels is found in these data which show that the critical sum of carbon and nitrogen for optimum toughness decreases rapidly with increasing chromium content, and except in the low ranges of chromium the sum of carbon and nitrogen that can be tolerated is less than the total amount of carbon and nitrogen normally present in such steels.

The curves in the drawing were derived from many tests made of steels varying in chromium content and in carbon and nitrogen contents. In such tests hot-worked samples of steels were subjected to Izod impact tests at room temperature and at temperatures above and below room temperature. The samples were heated for six hours at 900° C. and quenched in water before testing. Representative examples of results of these tests are given in the following tables. In Table I Izod impact values obtained at room temperature, —50° C. and —100° C. are set forth. In Table II are presented tensile test data taken at room temperature, tensile strength being measured in pounds per square inch, elongation (per cent El.) in percentage of a two-inch gage length, and "per cent R. A." is percentage reduction of area at fracture.

Table I

Composition—Remainder Fe					Izod impact—ft.-lb.		
Percent Cr	Percent Si	Percent C	Percent N	Percent other	Room temp.	−50° C.	−100° C.
20.55	([1])	0.013	0.003	Nil	89	98	[2] 15/47
21.79	([1])	.014	.002	Nil	92	90	100
23.56	([1])	.012	.016	Nil	97	102	[2] 7/33
25.44	([1])	.010	.001	Nil	96	100	51
25.13	([1])	.014	.003	Nil	100	100	100
28.17	([1])	.018	.002	Nil	90	N.T.	N.T.
31.24	([1])	.012	.007	Nil	91	N.T.	N.T.
34.75	([1])	.010	.002	Nil	69	91	6
37.37	([1])	.016	.004	Nil	80	N.T.	N.T.
25.13	0.01	.014	.003	Nil	100	100	100
25.70	.02	.018	.003	Nil	98	106	39
25.83	.14	.014	.002	0.04 Mn	100	106	116
26.41	.23	.018	.012	0.03 Mn	110	114	66
26	.24	.016	.003	Nil	90	106	116
25.18	.53	.005	.003	Nil	102	N.T.	5
25.55	.78	.005	.003	Nil	112	116	119
26.05	1.86	.008	.010	Nil	4	N.T.	N.T.
25	([1])	.004	.002	2 Mo	102	N.T.	N.T.
25	([1])	.003	.004	1 Ni	93	100	108
25	([1])	.006	.005	2 Ni	87	97	95
25	([1])	.004	.002	3 Ni	97	86	101

[1] No Mn or Si added, but traces of both probably present.
[2] Two specimens with different values.
N. T. means not tested.

Table II

Composition—Remainder Fe [1]				Tensile strength	Percent el.	Percent R. A.
Percent Cr	Percent C	Percent N	Percent other			
25.44	0.010	0.001	Nil	61,600	43	74
25.13	.014	.003	Nil	53,600	37	71
31.39	.016	.002	Nil	65,000	29	31
34.75	.010	.002	Nil	70,000	20	44
37.77	.016	.004	Nil	71,000	33	57
25	.003	.004	1 Ni	64,300	27	43
25	.006	.005	2 Ni	66,100	31	60
25	.004	.002	3 Ni	70,500	24	41

[1] No Mn or Si added, but traces of each probably present.

The data in Tables I and II illustrate the toughness attainable at room temperature and well below in ferritic chromium steels containing 20% to 40% chromium when the sum of their carbon and nitrogen contents is kept below the curves shown in the drawing. The data show further that by lowering the sum of carbon and nitrogen in such steels below the curve in the drawing the transition from toughness to brittleness is retarded and that in general, the lower the sum of carbon and nitrogen, the lower the temperature of transition from toughness to brittleness.

Reduction and control of carbon and nitrogen can be carried out by utilizing materials of very low carbon and nitrogen contents and by melting and casting the steel at a reduced pressure in contact with an oxygen-bearing material. Under the latter conditions, carbon can be oxidized in preference to chromium and the carbon monoxide gas which forms can be readily removed from the steel as it is not very soluble. The oxidation of carbon, however, only proceeds if the partial pressure of the carbon monoxide in the atmosphere over the steel is less than the equilibrium value at a given temperature. This means that to remove carbon from the steel the carbon monoxide gas produced in the carbon-oxygen reaction must be continuously pumped from the system. As the process of oxidizing carbon proceeds relatively slowly, sufficient time must be allowed after the charge is melted for the reaction to approach equilibrium.

The mechanism of nitrogen removal is best explained by Henry's law which states that the

partial vapor pressure of the solute is proportional to the mol fraction of the solute, which means that the solubility of a gas in a liquid decreases as the pressure is reduced. The reduction in nitrogen content of the steel is due to the lowering of the partial pressure of nitrogen over the bath.

To obtain the desired carbon and nitrogen levels it has been found necessary to keep the pressure less than about 1000 microns of mercury if excessive bath temperatures are to be avoided. The use of low pressures, therefore, has the added advantage of prolonging furnace refractory life. Excessive sublimation of chromium occurs with long holding at pressures of less than about 50 microns of mercury, and pressures in the range of 200 to 500 microns of mercury give best operating results.

Instead of melting the steel at a reduced pressure, the desired control or reduction of carbon and nitrogen may be attained by maintaining an inert atmosphere free from traces of nitrogen over the steel while melting. Argon or helium are ideal for this purpose as they are inert gases, but in using a gas atmosphere it is necessary to circulate purified gas continuously over the surface of the metal in order to prevent the partial pressure of nitrogen and carbon monoxide from building up in the inert atmosphere.

Small amounts of nickel, copper and cobalt, say up to 3% of nickel or cobalt and 2% copper, may be present in the 20% to 40% ferritic chromium steels of the invention without seriously altering their characteristics provided that the total carbon and nitrogen content is such that it falls below the curves in the drawing. Likewise, small amounts of other carbide-forming elements than chromium may be present, for instance up to 3% of molybdenum or tungsten, for improved corrosion resistance or high-temperature strength. The steels should be fully deoxidized, manganese and silicon being suitable deoxidizing agents, but for optimum toughness at low temperatures silicon should fall well below 1%, and the carbon and nitrogen contents as far below the critical level as possible. The amount of residual silicon should not greatly exceed that needed for deoxidation purposes. Silicon apparently tends to shift the temperature at which embrittlement occurs upwards, particularly if carbon and nitrogen are near the critical total and chromium is in excess of 25%. Manganese is difficult to retain if the steel is melted at pressures below about 4 mm. of mercury. However, if the steel is made under conditions favorable to the retention of manganese, it is suggested that manganese not exceed 1% maximum. Sulfur and phosphorus, usual impurities in steel, may be present, but phosphorus tends to shift the embrittlement temperature upward, and hence should be kept as low as possible. Other impurities in the raw materials may have a similar influence, and for optimum toughness at low temperatures, the purity of the steel should be kept high.

The very low carbon and nitrogen steels covered by this invention are capable of being welded. The steels should be welded under conditions such that nitrogen and carbon pick-up is avoided, or with austenitic electrodes such as 18% chromium-8% nickel steels or 25% chromium-20% nickel steels as the austenitic steels are not seriously susceptible to loss of toughness due to carbon and nitrogen pick-up during welding, and they will produce welds matching the good ductility and toughness of the base metal.

This application is in part a continuation of our application Serial No. 36,558, filed July 2, 1948, now abandoned.

What is claimed is:

1. A ferritic chromium steel containing 20% to 40% chromium, up to 3% nickel, up to 3% cobalt, up to 2% copper, up to 3% molybdenum, up to 3% tungsten, the remainder, except for incidental impurities, being iron, carbon and nitrogen, the sum of the carbon and nitrogen contents for a selected chromium content being no greater than the value determined by the intersection of the plot of the selected chromium content with the curve AB of the drawing, said steel having in the annealed condition an Izod impact strength of at least 18 foot pounds at room temperature.

2. A ferritic chromium steel containing 20% to 40% chromium, up to 3% nickel, up to 3% cobalt, up to 2% copper, up to 3% molybdenum, up to 3% tungsten, the remainder, except for incidental impurities, being iron, carbon and nitrogen, the sum of the carbon and nitrogen contents for a selected chromium content being no greater than the value determined by the intersection of the plot of the selected chromium content with the curve CD of the drawing, said steel having in the annealed condition an Izod impact strength of at least 18 foot pounds at room temperature.

3. An article which in its normal use is required to withstand corrosion and to have high toughness at ordinary room temperatures, said article being composed of a ferritic chromium steel containing 20% to 40% chromium, up to 3% nickel, up to 3% cobalt, up to 2% copper, up to 3% molybdenum, up to 3% tungsten, the remainder, except for incidental impurities, being iron, carbon and nitrogen, the sum of the carbon and nitrogen contents for a selected chromium content being no greater than the value determined by the intersection of the plot of the selected chromium content with the curve AB of the drawing, said steel having in the annealed condition an Izod impact strength of at least 18 foot pounds at room temperature.

4. An article which in its normal use is required to withstand corrosion and to have high toughness at ordinary room temperatures, said article being composed of a ferritic chromium steel containing 20% to 40% chromium, up to 3% nickel, up to 3% cobalt, up to 2% copper, up to 3% molybdenum, up to 3% tungsten, the remainder, except for incidental impurities, being iron, carbon and nitrogen, the sum of the carbon and nitrogen contents for a selected chromium content being no greater than the value determined by the intersection of the plot of the selected chromium content with the curve CD of the drawing, said steel having in the annealed condition an Izod impact strength of at least 18 foot pounds at room temperature.

5. A welded article which in its normal use is required to withstand corrosion and to have high toughness at ordinary room temperatures, said article being composed of a ferritic chromium steel containing 20% to 40% chromium, up to 3% nickel, up to 3% cobalt, up to 2% copper, up to 3% molybdenum, up to 3% tungsten, the remainder, except for incidental impurities being iron, carbon and nitrogen, the sum of the carbon and nitrogen content for a selected chromium content being less than the value determined by the intersection of the plot of the selected chromium content with the curve AB of the drawing, said steel having in the annealed condition an Izod impact strength of at least 18 foot pounds at room temperature.

6. A welded article which in its normal use is required to withstand corrosion and to have high toughness at ordinary room temperatures, said article being composed of a ferritic chromium steel containing 20% to 40% chromium, up to 3% nickel, up to 3% cobalt, up to 2% copper, up to 3% molybdenum, up to 3% tungsten, the remainder, except for incidental impurities, being iron, carbon and nitrogen, the sum of the carbon and nitrogen contents for a selected chromium content being less than the value determined by the intersection of the plot of the selected chromium content with the curve CD of the drawing, said steel having in the annealed condition an Izod impact strength of at least 18 foot pounds at room temperature.

WILLIAM O. BINDER.
RUSSELL FRANKS.

REFERENCES CITED

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

Transactions, American Society for Metals, vol. 23, page 33, published by the American Society for Metals, Cleveland, Ohio.