Feb. 13, 1951 W. L. BESSELMAN ET AL 2,541,857

CONTROL OF CONSTITUENT-POTENTIALS

Filed May 30, 1945 2 Sheets-Sheet 1

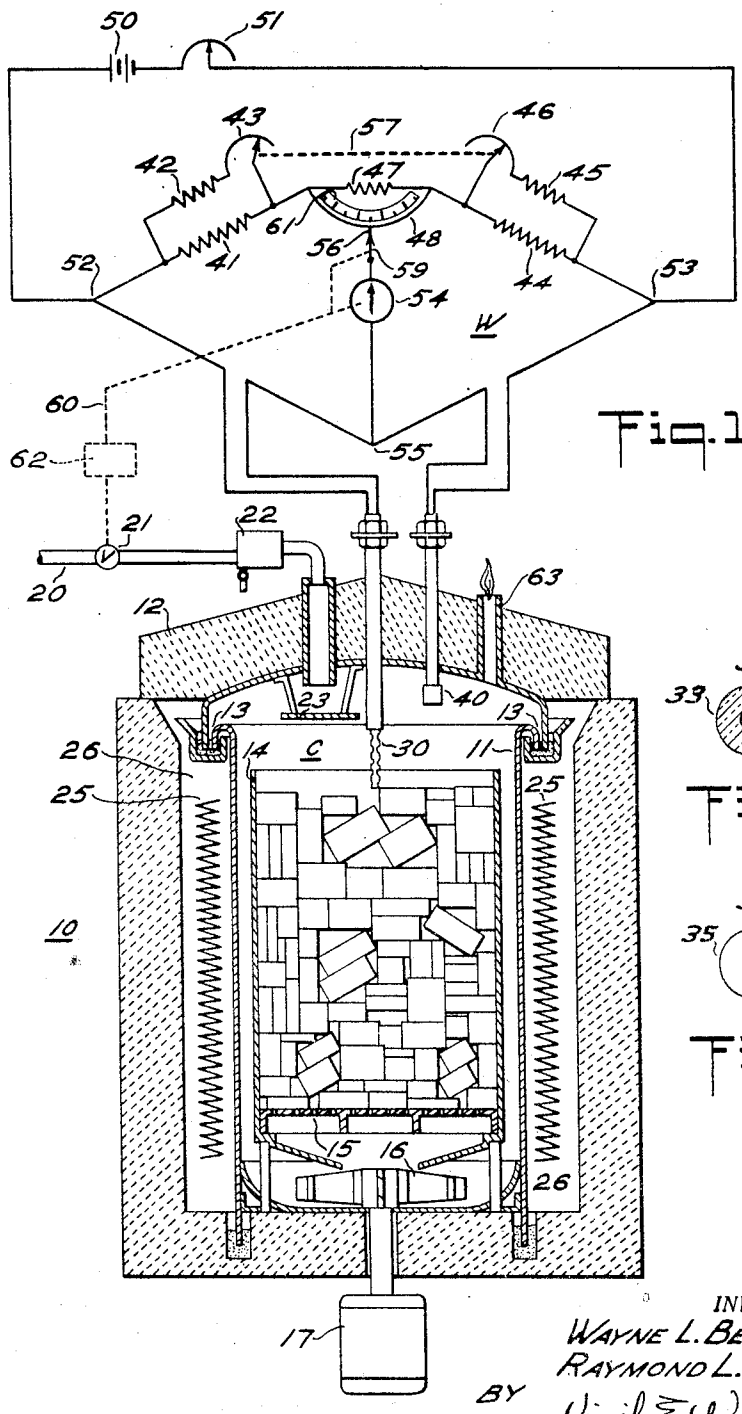


Fig. 1.

Fig. 2A

Fig. 2B.

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Filed May 30, 1945 2 Sheets-Sheet 2

Fig. 3.

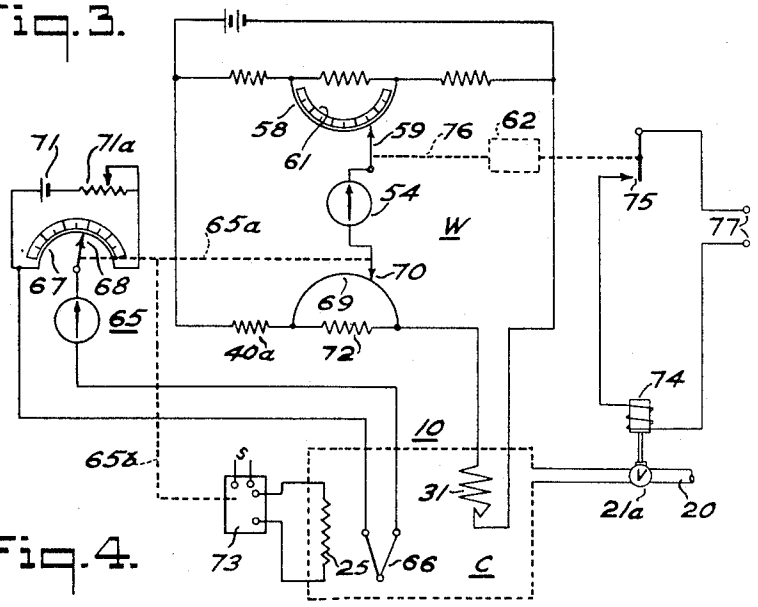


Fig. 4.

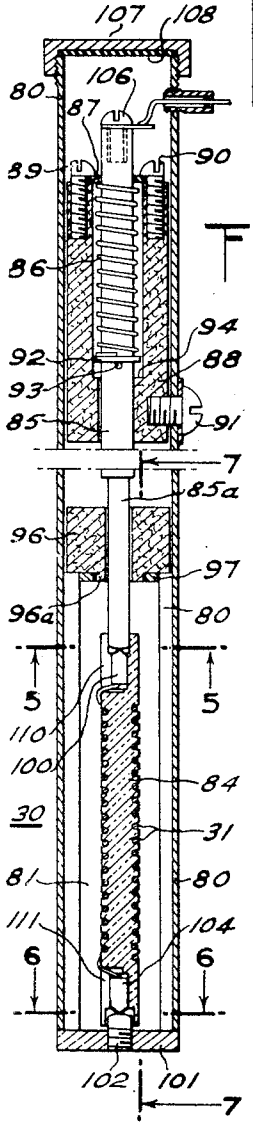


Fig. 5.

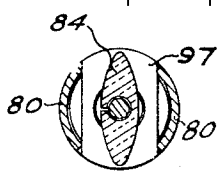


Fig. 6.

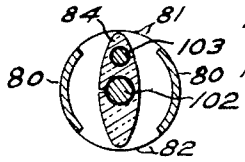


Fig. 7.

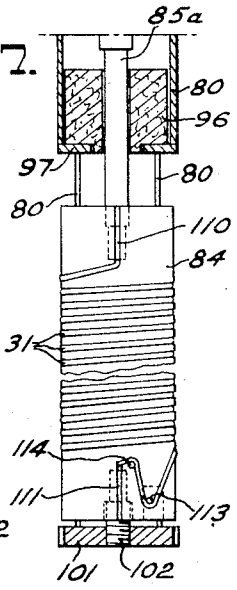
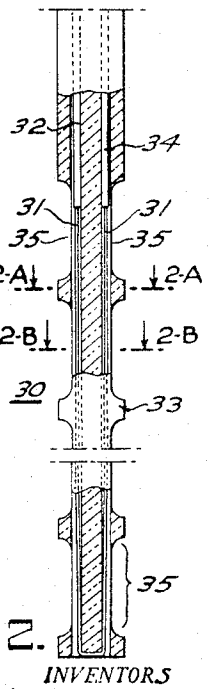


Fig. 2.



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2,541,857

CONTROL OF CONSTITUENT POTENTIALS

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Application May 30, 1945, Serial No. 596,792

12 Claims. (Cl. 266—2)

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This invention relates to an apparatus for determining the constituent-potential of gases, more particularly to the determination of the constituent-potential with respect to work undergoing treatment by gases such as in carburizing or nitriding of metals, and has for an object the provision of a system in which the constituent-potential may be determined coincidentally with the treatment of the work.

Heretofore it has been proposed to measure carbon pressures or potentials by utilizing a very fine carbon steel wire which is heated by electric current flowing therethrough to a temperature of the order of 800° C. to 1100° C. while subject to a stream of carburizing gases. After equilibrium has been established, the wire is rapidly cooled to produce a martensitic structure. Thereafter the resistance of the wire is measured. It has been stated that there is correlation between the resulting resistance of the wire and the carbon content thereof, providing the wire upon cooling is completely in the martensitic phase.

Systems of the foregoing type have many disadvantages. They require separate treating chambers, and they do not permit continuous measurement of constituent-potentials. In consequence, they are not suited for continuous automatic control of gaseous treating mediums.

The term "carbon-potential" and the broader term "constituent-potential" are herein used to denote a unit or factor which expresses the extent of transference of carbon from a gas into work, or transference of carbon from the work to the gas. Since this same phenomenon is also present as between nitrogen and steel, and between other gases and metals, the broader term "constituent-potential" is intended to denote the transference and the possibility of transference of material between a gaseous medium and the work subjected thereto, which transference varies the composition of the case, the latter meaning the surface and near-surface region affected by said transference.

In accordance with the invention, there is provided a system of not only measuring the constituent-potential of an atmosphere but also one in which the said potential of the atmosphere may be continuously measured and controlled and which by integration of all the variables of the process may be utilized to predetermine the ultimate compositional characteristic of work as affected by the atmosphere.

In carrying out the invention in one form thereof, a wire or filament of iron, or an alloy thereof, is disposed adjacent the work and both are subjected to the same temperature and atmosphere. The variation in an electrical characteristic, the resistance, of the wire or filament is measured and is utilized to indicate the constituent-potential of the gaseous medium or atmosphere.

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For a more complete understanding of the invention and for further objects and advantages thereof, reference should be had to the accompanying description, taken in conjunction with the drawings, in which:

Fig. 1 diagrammatically illustrates the invention in one form as applied to a carburizing furnace for the measurement and control of constituent-potentials;

Fig. 2 is a longitudinal view, partly in section, of a part of the detecting element 30 of Fig. 1;

Fig. 2–A is a sectional view taken on the line 2A—2A of Fig. 2;

Fig. 2–B is a sectional view taken on the line 2B—2B of Fig. 2;

Fig. 3 is an alternative arrangement for the measurement of control of constituent-potentials;

Fig. 4 is a longitudinal view, partly in section, of a modified form of detecting element;

Figs. 5 and 6 are sectional views taken respectively on the lines 5—5 and 6—6 of Fig. 4; and

Fig. 7 is a fractional side elevation, partly in section, of Fig. 4.

Referring to the drawings, the invention in one form has been illustrated as applied to a carburizing furnace 10 of the type disclosed in Harsch Patent No. 2,161,162. Though treating chambers or carburizing furnaces of other construction may be utilized, the one disclosed in said Harch patent has been found to be satisfactory. For a detailed description of the structure and the carburizing process in general, reference may be had to said patent. Briefly, the carburizing furnace 10 consists of a reaction chamber C defined by a retort 11 and a cover 12, a seal 13 being provided between the cover and the retort. The work or load, though it may be a single piece, has been illustrated as comprising a group or batch of pieces disposed haphazardly in a basket 14. This basket is provided with a perforated plate or grid 15. A fan 16, driven by a motor 17, forcibly circulates through the load hot vehicle gases which serve as a carrier for the carburizing components or constituents of the furnace atmosphere.

The carburizing agent, in liquid, gaseous, or vapor phase, is supplied to the reaction chamber C by way of an inlet pipe 20, under the control of a valve 21, and after passing through a dehydrator 22 is directed against a distributor plate 23. The hot vehicle gases swirl about in the space below the cover and above the work and entrain and distribute the freshly introduced agent quickly to bring it to dissociation temperature.

The work pieces and the vehicle gases are heated to carburizing temperature, usually in the neighborhood of about 1700° F. in any suitable manner, such, for example, as by electrically heated resistors 25 disposed in the heating chamber 26 which surrounds the retort 11. The car-

burizing agent is quickly heated to a temperature to cause cracking or dissociation thereof, to yield an atmosphere having the desired constituent or carbon-potential with respect to the steel or ferrous metal parts of the load. It is important to the Harsch system of carburizing that the carburizing agent shall be introduced into the carrier gas at a point such that the agent reaches the cracking temperature as it approaches the work. In consequence, the carburizing action takes place with the reaction products in their nascent state.

It is to be understood the present invention is applicable to systems other than as shown by said Harsch patent, for example, to systems where the carburizing agent is given a preliminary or final cracking outside of the reaction chamber.

In accordance with the invention, the constituent or carbon-potential of the gaseous medium toward the work is determined by means of an element 30 which includes a relatively small iron wire or filamentary metal 31, Fig. 2, capable of absorbing and giving up the constituent intended for exchange between the retort atmosphere and the work. For a wire or filament of rectangular cross section, the shorter cross-sectional dimension should be small. A round wire of relatively small size also presents a short path for transference of material.

In accordance with one form of the invention, the sensitive or detecting element 30 may comprise a 12'' length of No. 30 A. W. G. iron wire 31 of the following composition:

	Per cent
Carbon	.06
Manganese	.23
Phosphorus	.017
Sulphur	.043
Silicon ---- less than	.003
Nickel	.047
Chromium ---- less than	.01
Copper	.123
Tin ---- less than	.01
Iron	99.46

This particular ferrous alloy is one which is used quite extensively in thermocouples, as described in Finch Patent No. 2,325,759. Though ferrous alloys of widely differing composition may be utilized, the one specifically disclosed is preferred because of its availability and because of the need to provide replaceable elements of the same composition. This wire 31 is connected at one end to a conductor 32 and extends downwardly through a porcelain or other refractory support 33, Figs. 2, 2–A and 2–B, around the end thereof and upwardly to a second conductor 34. The ceramic rod 33 is provided with a series of elongated recesses or openings 35 which expose the wire to the furnace atmosphere.

A 12-inch length of the foregoing wire at a temperature of 77° F. has a resistance of 0.73 ohm. The element 30 is disposed in the reaction chamber C in a position to be subjected to the same gases and temperature as the work. Both the wire 31 and the work are coincidentally subjected to transference of material to and from the gases. Carbon is absorbed or given up by the wire 31 until equilibrium conditions are attained. These equilibrium conditions are rapidly established because of the short carbon path through the wire or filament 31. In accordance with the invention, it has been discovered that an electrical characteristic of the filament or

wire 31, the resistance thereof, will vary to a degree dependent upon the amount of carbon or other constituent taken up or removed from the wire. For example, at a temperature of 1700° F. the resistance of the wire 31, with 0.2% carbon therein, will be 6.95 oms; for the same temperature a similar wire with a carbon content of 1.00% will have a resistance of 7.21 ohms.

In the preferred form of the invention the sensitive element 30, including the wire 31, is at all times subjected to the same ambient conditions as that of the work, and coincidentally therewith. In consequence, not only is a determination of the character of the atmosphere possible but also there is provided a means for controlling or regulating the character of the atmosphere within the reaction chamber C. In accordance with the invention, the foregoing variations in the resistance of the wire 31, at high temperature, occur with compositional changes in the wire itself. Contrary to prior knowledge and belief there are provided new and valuable methods and means of controlling the atmosphere within the reaction chamber C. Stated differently, it has been discovered that the electrical resistance of the wire 31 varies though the wire has an austenitic structure; that is, with the carbon thereof largely in a free state, or in solid solution. The resistance, other factors remaining the same, is at all times dependent upon the carbon present in the wire or filament 31. It has also been discovered that with the wire 31 heated to temperatures of 1000–1100° F., the same property of varying resistance is exhibited with respect to nitrogen. Hence, the invention is applicable to nitriding purposes and the like.

The simplified form of a measuring system illustrated in Fig. 1, consists of a network in the form of a Wheatstone bridge W in which one arm thereof comprises the iron wire 31 while a second arm thereof includes a sealed element 40 having within the interior a suitable length of wire having the same resistance-temperature coefficient as the wire 31. It may be of the same material as wire 31, though wire or wires of differing material but with the same temperature-coefficient of resistance may be used. It is sealed within the container 40 to isolate it from the atmosphere of the reaction chamber C. By connecting this resistor in the second arm of the Wheatstone bridge, automatic compensation is introduced therein for changes in resistance of the wire 31 due solely to temperature changes. It has been found that the resistance of the wire 31 varies substantially linearly with temperature for temperatures above around 1400° F. The temperature coefficient of resistance for practically any carbon content, at least between 0.25% to 1.25%, is 0.018% per degree F.

A third arm of the bridge W includes resistors 41 and 42 and a slidewire 43, while the fourth arm of the bridge includes resistors 44 and 45 and the slidewire 46. A resistor 47 and a slidewire 48 are provided between the last-named arms of the bridge. A suitable source of current, as the battery 50, is connected through a variable resistor 51 to the conjugate points 52 and 53 while a sensitive detecting instrument 54 is connected between the conjugate points 55 and 56. The slidewires 43 and 46 are simultaneously and oppositely adjustable and are preferably mechanically connected together as illustrated by the broken line 57. By adjusting the slidewires 43 and 46 to shift resistance from one arm of the bridge W to the other, adjustment for variation

in the circuit constants, particularly the cold resistance of element 30, may be made.

The detecting instrument 54 includes a sensitive galvanometer and a mechanical relay preferably of the type fully disclosed in Squibb Patent No. 1,935,732. Reference may be had to said Squibb patent for details of the galvanometer and mechanical relay. Reference may also be had to Lane Patent No. 2,119,108 for disclosure of a mechanical relay system suitable for operation or control of the valve 21.

Inasmuch as it has been discovered that the resistance of the wire 31, when in equilibrium with the atmosphere surrounding it, varies with the carbon or constituent-potential of that atmosphere, the slidewire 48 associated with the mechanical relay and the chart or scale thereof (not shown) may be calibrated directly in terms of carbon content in the surface of a particular steel, or in terms of the carbon content of a thin shim steel of composition, for example, S. A. E. 1010, known as shim steel. In Fig. 1, the scale 61 is illustrated and it will be assumed it is so calibrated. In operation, the slidewires 43 and 46 will be preset to positions to calibrate the bridge W in terms of the carbon content indicated by scale 61. The resistors 25, of the furnace 10, will be energized to produce the desired temperature, generally around 1700° F., within the reaction chamber C. Under the control of the instrument 54, the valve 21 will be opened to a degree which permits the entry into the chamber C of a sufficient quantity of a carburizing medium which, upon contact with the wire 31, will add to or subtract carbon from the wire until the composition thereof is at a selected value. The instrument 54, through valve 21, continues to control the atmosphere within the chamber C so as to maintain constant the composition of the wire 31. Accordingly, both a continuous measurement and control of the carbon or constituent-potential of the atmosphere are provided.

The shaft 10 of the Sqibb Patent 1,935,732 may directly control valve 21 or it may indirectly control that valve. In either case, adjusting means 62 are provided to change the actuation of the valve with respect to the relative positions of the contact 59 and the slidewire 48. This adjusting means in simple form may comprise a lengthening and shortening means for the linkage indicated by the broken line 60. In this manner, any predetermined constituent-potential of the atmosphere within reaction chamber C may be maintained.

A duration-type of control as disclosed in Davis Patent No. 2,325,232, particularly Fig. 3, has been found satisfactory. The slidewire 3 thereof will comprise adjusting means 62, while slidewire 39 of the patent will correspond with slidewire 48 of Fig. 1 hereof. By changing the relative positions of the adjusting means 62 (slidewire 3 of the patent) and slidewire 48 (slidewire 39 of the patent) the carbon-potential may be preset or selected at any disired value. The valve 124 of the patent will, of course, be replaced by the valve 21 of Fig. 1 hereof.

In the foregoing description it is to be understood that in theory neither the length of the filament 31 nor its cross-sectional area is significant. It may be of any desired length. It may have any desired cross-sectional area. However, in practicing the invention, the smaller the lesser cross-sectional dimension is, the faster will equilibrium be reached with a given potential of the atmosphere. The cross-sectional characteristic, however, is preferably one which may be defined as including one dimension which is small for rapid equilibration of the constituent in the filament 31 and in the gaseous medium. In the preferred forms of the invention, satisfactory operation has been obtained with round wires varying in diameter from 0.003" to 0.040". Ribbons of similar thicknesses are likewise satisfactory. In the foregoing example, the wire 30 had a diameter of 0.010".

In carrying out the invention in one form thereof, a plurality of work pieces of the same composition were placed in the reaction chamber C and the controller was set for the maintenance or production in the case or surface layers of the work pieces of 0.65% carbon, as by the adjusting means 62. The heating resistors 25 were then energized to maintain the reaction chamber at a temperature of 1450° F. At intervals during a period of approximately twenty-four hours samples were removed through the outlet or vent pipe 63. These samples, upon analysis, had a case, or a surface and subsurface composition of between 0.65% and 0.66% carbon.

The foregoing procedure with like work pieces within the reaction chamber C was then repeated for a second 24-hour run, with the temperature of the reaction chamber C at 1750° F. Again, work pieces removed at intervals during this run showed a case between 0.64% and 0.66% carbon. Though the temperature had been increased by 300°, the carbon content of the case of all work pieces was closely held between the limits of 0.64% and 0.66%. The carbon content throughout the 24-hour runs was maintained fully as closely as quantitative analyses of carbon content can be made.

With like samples of work pieces, the adjusting means 62 was then set for a carbon content of 0.50%. For one run the temperature of the reaction chamber C was maintained at 1450° F. and for another run it was maintained at 1750° F. All samples withdrawn at intervals during each run showed a carbon content within the range of 0.47% to 0.52%. Additional tests were made, with like work pieces or samples, for runs respectively at 1450° F. and 1750° F. but with the adjusting means 62 set for a carbon content of 0.85%. Again, the samples removed at intervals during each run showed a carbon content which ranged from 0.85% to 0.90%.

The foregoing exemplary tests demonstrate an accuracy of control which has heretofore been unattainable and by means of which accurate control of carburizing at different temperatures has been made possible.

It is not essential that a second tube element 43 be provided in a sealed container. In accordance with a further preferred modification of the invention, Fig. 3, automatic compensation for changes in the temperature of the reaction chamber C may be provided by means of a detecting instrument 65 which is preferably of the type disclosed in the aforesaid Squibb Patent No. 1,935,732. The instrument 65 operates in response to the temperature of a thermocouple 66 disposed within the chamber C and not only serves relatively to adjust a slidewire 67 with respect to its contact 68 but also to effect, through mechanical connection 65a, relative adjustment between a slidewire 69 and its contact 70. The slidewire 67 in conjunction with a source of supply such as a cell 71 and resistor 71a forms a potentiometer which, under the control of the device 65, provides a potential to balance that

produced by the thermocouple 66. The slidewire 69 and its associated resistor 72 introduce a correction into the Wheatstone bridge W to correct for the variation with temperature of the resistance of the filamentary metal or wire 31, that is, the combined resistance of resistor 72 and slidewire 69 is so varied as to compensate for the temperature component of the resistance variation of the filamentary metal or wire 31. Hence, the network W will respond only to the change in the compositional component of the resistance variation of said filamentary metal or wire 31.

If the temperature of the reaction chamber C is maintained constant, automatic compensation for changes in temperature of the wire 31 need not be provided. In such case, the temperature-responsive element 40 may be replaced with a resistor having a negligible temperature coefficient of resistance, such as "Manganin," located outside the furnace.

The instrument 65, through mechanical connection 65*b*, also serves to control, by means of controller 73, the energization of the heating resistors 25 to maintain a predetermined temperature within chamber C. It will be noticed there has been substituted for the element 40 of Fig. 1, a fixed resistor 40*a*. Further variation, in accordance with Fig. 3, is the provision in supply line 20 of a control valve 21*a* which is operated by a solenoid 74 under the control of contacts 75. Whenever the instrument 64 detects a deviation in the carbon content it will be understood that an adjustment is made between the slidewire 58 and its associated contact 59. It will be assumed the adjusting means 62 is set for a carbon content of 0.75% which value will be assumed to produce balance of network W with the contact 59 in the position illustrated in Fig. 3. If the carbon content should be less, the unbalance of the network will cause the contact 59 to move to the left with respect to the scale 61 (or the scale and slidewire to move to the right). This movement will, through connection 76 and adjusting means 62, close contacts 75 to energize solenoid 74, from source 77, thereby to open the valve 21*a*. Accordingly the flow of carburizing material to the chamber C will be increased. As the carbon content in wire 31 rises to the predetermined value of 0.75%, balance of network W will be re-established with the parts again in the illustrated positions. Should the carbon content rise to above the selected value, the contacts 75 will remain open. The valve 21*a* will remain in a more or less closed position. Because of air infiltration, the carburizing atmosphere will be diluted so as to decrease the carbon or constituent-potential thereby to decrease the carbon content of the work pieces. If more positive control is desired, a diluent such as nitrogen may be introduced under control of mechanical connection 76.

The carburizing fluid introduced into the furnace by way of pipe 20 and valve 21*a* may be of the type disclosed in the aforesaid Harsch Patent No. 2,161,162. It is to be further understood that the concentration of carbon in the surface of a metal quickly assumes an equilibrium value, notwithstanding the fact the carbon will continue to be transferred through the surface layer in order to establish a like concentration in the subsurface or interior of the metal. By utilizing a filamentary means having one cross-sectional dimension small, this equilibrium is attained without undue delay. After the foregoing equilibrium is attained, the carbon content at the surface and throughout the wire 31 will not change as long as the given conditions are maintained. The depth of the case on the work pieces will vary as a function of time and temperature but the carbon content at the surface and subsurface will be maintained as above described.

The same principles may be likewise applied to other processes. For example, a wire of iron or of an iron alloy when exposed to a nitrogen-bearing atmosphere will gain or lose nitrogen. As in the case of carbon, there will be a nitrogen or constituent-potential as between the nitrogen and the work which in general consists of alloys of the type known to those skilled in the art as "Nitralloy." As applied to a nitriding process, and utilizing a wire 31 of the same character as above described, the resistance of the wire 31 varied through an even greater range than for carbon.

As between carburizing and nitriding, one of the principal differences is that in carburizing a certain amount of air infiltration is permitted, though separate streams of air, steam, or a decarburizing medium may be utilized when desired. In contrast, during nitriding the reaction chamber is ordinarily sealed to exclude air infiltration. To dilute the nitriding atmosphere a second stream of an inert gas such as nitrogen may be utilized. The nitriding gas itself is preferably ammonia.

The sensitive element 30 may also take the form illustrated in Figs. 4–7. As shown, an outer tubular housing 80, of a chromium-nickel alloy of the type known under the trade name "Chromax," is provided at its lower end with openings 81 and 82 to expose to the furnace atmosphere the wire 31 which is wound on a ceramic core 84. The core 84 is of oval shape, as best shown in Figs. 5 and 6. The construction of Fig. 4 has the advantage that the core 84 and the wire 31 comprise a removable unit. It is held in place by means of a plunger 85, preferably of nickel, biased downwardly by a compression spring 86. The upper end of this spring bears against a collar or washer 87 secured to an inner support 88 of a ceramic material known as "Transite" by means of screws 89 and 90. The block itself is held in place by a screw 91 which extends through the housing 80. The lower end of the spring 86 bears against a washer 92 supported on a pin 93 carried by the plunger 85. Downward movement of the washer 92 and spring 86 is limited by engagement of the pin 93 or washer 92 with the shoulder 94 provided on the support 88.

The lower end 85*a* of the plunger is of reduced size and passes through an opening in a guiding block 96. This block has a lower end 96*a* of reduced size which extends into a plate 97 welded at its ends to the housing 80, as best shown in Fig. 7. The lower end of plunger 85 bears against a contact plug 100 to which the upper end of wire 31 is fastened, as by welding. The pressure of spring 86 is applied from plunger 85 to plug 100 to insure a good electrical contact.

From the bottom closure 101, two studs 102 and 103, Figs. 4 and 6, extend into complementary openings provided in the ceramic core 84. These studs hold the core 84 in the illustrated position. The upper end of the stud 102 bears against a second contact plug 104 to which the opposite end of wire 31 is suitably attached, as by welding. Thus, the spring 86 is effective to press the core 84 downwardly against plug 104 which in turn presses against stud 102 to make a good elec-

trical contact therewith. Hence, one of the conductors of network W leading to wire 31 may be attached to plunger 85, as by the screw 106, while the other conductor may be attached to the housing 80, as at the screw 91; or otherwise. The upper end of the housing 80 is provided with a screw cap or closure 107 and a sealing gasket 108.

To remove the sensitive unit comprising wire 31 and support 84, the body portion is moved upwardly against the bias of the spring 86 until the lower end clears or is free of the studs 102 and 103. The support 84 is then moved outwardly through one or the other of openings 81 and 82. The same, or another unit may be inserted in the supporting means by carrying out the described procedure in reverse order.

As shown, the opposite ends of the core 84 are provided with slots 110 and 111 which extend from one side of the core inwardly for communication with the end-recesses thereof. These slots 110 and 111 also communicate with the recesses of smaller diameter into which the contact plugs 100 and 104 are disposed. If after the assembly as a whole has been removed it is desired to replace the wire 31, this may be accomplished by unhooking the wire from the pins 113 and 114. Enough slack must be provided to permit the withdrawal of the plug 104 and for the removal of the wire through the slot 111. After the wire has been unwound from the core 84, it, and the contact plug 100, are then lifted upwardly through the slot 110. A new wire may be wound in place by repeating the foregoing steps in the reverse order. New elements do not need to be frequently provided, particularly if care is taken in withdrawing the element from the reaction chamber C. To this end, the element may preferably enter the reaction chamber C through an exit pipe, similar to pipe 63, Fig. 1. By withdrawing it slowly through carbonaceous gases in the exit pipe, they not only cool the element, including the wire 31, but also prevent oxidation which would otherwise render it useless for later use. In the absence of carbonaceous gases, the element is rapidly withdrawn quickly to cool the wire 31, thereby to minimize oxidation thereof.

In summary, there has been provided a continuous control system, based on measurements made continuously during operation of the process. This means that through the period when the temperature and the atmosphere is such as to affect the work, the element 30 will be affected coincidentally therewith. There has, therefore, been provided a means for processing work at any temperature practical for the process. The system also makes possible the protection of the work during cooling in the furnace before discharge therefrom. Upon this latter aspect, by controlling the atmosphere, the work may be protected during cooling from loss of the material previously added thereto.

Though the principles of the invention have been fully set forth above, the following additional information is set forth as a further guide to those skilled in the art. Though these data are presented in connection with a sensitive element of iron, a term used to include materials largely composed of iron and which also includes carbon steels and some low alloy steels, the invention may also be applied to other ferrous materials with respect to which a constituent-potential exists as between a treating atmosphere and work exposed thereto.

In the following Table I there is comprehensively set forth the relationship between the resistance of a one-foot length of the wire 31 and the carbon content of a particular steel at four different temperatures:

TABLE I

Carbon content of Shim Steel (S. A. E. 1010) vs. element resistance

Element Resistance, Ohms	1,450 ° F.	1,550 ° F.	1,650 ° F.	1,750° F.
	per cent carbon			
6.65	.122			
6.7	.255			
6.75	.390	.069		
6.8	.526	.203		
6.85	.662	.337	.015	
6.9	.797	.473	.150	
6.95	.930	.607	.283	
7.0	1.067	.742	.417	.090
7.05	1.201	.875	.552	.224
7.1		1.010	.685	.358
7.15		1.143	.819	.494
7.2		1.277	.953	.627
7.25			1.089	.762
7.3			1.223	.895
7.35				1.030
7.4				1.165

In Table II there are set forth the respective carbon contents in the steel of Table I and in the surface layers of eight different steels at four different temperatures, the steels being designated A, B . . . G inclusive, and whose compositions, as well as the steel of Table I, are given in Table III.

TABLE II

Carbon contents of steels, per cent

"Shim"	A	B	C	D	E	F	G
			1450° F.				
0.40	.359	.419	.110	.555	.338	.412	.372
.50	.454	.542	.192	.674	.423	.515	.474
.60	.550	.668	.272	.793	.510	.619	.577
.70	.647	.789	.353	.912	.595	.721	.677
			1550° F.				
.30	.278	.320	.269	.355	.224	.300	.284
.40	.374	.425	.355	.470	.368	.385	.375
.50	471	.533	.443	.587	.396	.470	.468
.60	.569	.639	.531	.703	.481	.556	.560
.70	.665	.746	.618	.820	.567	.642	.653
			1650° F.				
.30	.245	.345	.262	.323	.210	.258	.272
.40	.365	.443	.353	.438	.315	.377	.374
.50	.478	.543	.448	.551	.415	.491	.474
.60	.585	.643	.543	.667	.507	.603	.577
.70	.684	.741	.638	.781	.599	.710	.676
.80	.774	.838	.731	.898	.687	.812	.773
.90	.861	.929	.824	1.010	.771	.910	.871
1.00	.943	1.037	.919		.857	1.008	.963
1.10	1.025	1.139	1.012		.942	1.105	1.055
			1750° F.				
.30	.278	.303	.271	.333	.247	.268	.270
.40	.374	.412	.360	.430	.312	.365	.363
.50	.470	.524	.450	.534	.382	.464	.455
.60	.566	.628	.541	.640	.460	.565	.550
.70	.660	.731	.632	.748	.541	.668	.645
.80	.752	.830	.723	.853	.629	.773	.743
.90	.842	.926	.814	.988	.720	.878	.845
1.00	.932	1.019	.906	1.120	.815	.990	.949
1.10	1.021	1.104	.999	1.259	.915	1.102	1.051

TABLE III

Composition of alloy steels of Table II in per cent [1]

	Shim Steel SAE-1010	Drill Rod A	Ketos B	Solar C	SAE-52100 D	SAE-2515 E	SAE-3312 F	SAE-4615 G
Carbon	0.05–0.15	0.90–1.00	0.90	0.50	0.95–1.10	0.10–0.20	0.17 Max.	0.10–0.20
Manganese	0.30–0.60	0.20	1.25	0.40	0.20–0.50	0.30–0.60	0.30–0.60	0.40–0.70
Nickel						4.75–5.25	3.25–3.75	1.65–2.00
Chrome			0.50		1.20–1.50		1.25–1.75	
Molybdenum				0.50				0.20–0.30
Tungsten			0.50					
Silicon				1.00				

[1] Remainder iron.

By referring to Tables I and II, it will be readily apparent that if a case on the work is to have a carbon content of a particular value at a selected temperature, this carbon content is determined with respect to the particular steel and the corresponding carbon content of the shim steel.

A substantial part of the research work underlying this invention was conducted on "Shim Steel" (SAE—1010). Typical data are presented in Table I. The results, as shown in Table I, were then correlated in terms of tests made on other steels, as shown in Table II.

If it is desired to produce a case, or carbon content of approximately 100 points, one per cent, in the surface layer of the steel D at 1750° F., reference will first be made to Table II. It will be noted that a carbon content of 0.988% will be attained under those conditions which will give a carbon content of 0.90% in the "Shim Steel."

Reference is now made to Table I. The value 0.895% at 1750° F. will be taken as approximately the 0.90% value. The resistance of the element 31 for the value 0.895% will be 7.3 ohms at 1750° F.

It will be remembered that the scale 61, Figs. 1 and 3, is calibrated in terms of the carbon content of the shim steel. Hence, the slidewire 48, Fig. 1, or 58, Fig. 3, may be set directly to correspond with the carbon content 0.90%. The temperature of the chamber C is then maintained at 1750° F. for time determined by the depth of the case desired. A case will then be produced having a carbon content closely approximating the desired value of one per cent. The carbon content will be predetermined to within the accuracies now attainable with known methods of quantitative analyses. If the slidewires 48 and 58 are not calibrated in terms of carbon content, the resistance values of Table I may be referred to.

It will be recalled that the resistance of the wire 31 varies substantially linearly with temperatures above around 1400° F. This is above the critical temperature of the wire 31. Further, in accordance with the invention, the carbon content or constituent-potential may be continuously determined for operating temperatures below approximately 1400° F. by utilizing alloys of iron having lower critical temperatures than the example above set forth. More specifically, for the lower temperatures, the wire 31 may consist of an alloy of the following composition: nickle 1.65–2%, molybdenum 0.2–0.3%, manganese 0.4–0.7%, carbon 0.1–0.2%, with the remainder iron. With this alloy, the critical temperature will be 50° lower and therefore may be used for operations at temperatures around 1350° F.

In accordance with another aspect of the invention, it has been discovered that in the reducing atmosphere which exists in the treating chamber the contact elements 100 and 85*a* and the associated contacts 102 and 104 weld together. Upon initial installation of a sensitive unit 30 the parts will of course be clean and the contact resistance will be low. Because of the carbon-laden atmosphere one skilled in the art might expect that the contact resistance might change during operation. Because of the aforesaid phenomenon the contact resistance does not change. It remains constant and the union in the nature of a weld between the contacts not only assures continuing stability in the resistance of the contacts, but it also prevents change in the resistance due to vibration of the sensitive element 30 including those contacts.

While preferred embodiments of the invention have been described, it will be understood that further modifications may be made without departing from the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. In a high temperature metal-treating system in which work is subjected to a gaseous medium having a constituent which gives rise to a constituent-potential towards the work, means for determining said constituent-potential comprising a filamentary ferrous metal so disposed with respect to said work as to be subject to the same temperature and gaseous treating conditions thereof, and having a composition such that said constituent-potential with respect thereto is related to said constituent-potential towards said work, said filamentary metal having at least one cross-sectional dimension of a size which produces rapid equalization of said constituent-potential by change in the composition thereof, a balanceable network including means for connecting said filamentary metal in one branch thereof, a second filamentary metal, means for connecting it in a second branch of said network, means for sealing said second filamentary metal from said medium and for supporting it in heat-transfer relation with said medium, and means operable solely in accordance with change in the electrical resistance of said first-named filamentary metal due to compositional changes thereof for unbalancing said network for indicating during the treatment of work by said gaseous medium of said constituent-potential with respect to said work.

2. In a metal-treating system in which work is subjected to a gaseous atmosphere having at least one constituent which during treatment of the work is capable of transference to and from the medium and the work, a measuring network including a filamentary ferrous metal disposed

within said atmosphere and whose resistance varies with its temperature and with the composition of said atmosphere and a resistor in said network whose resistance varies solely with the temperature of said atmosphere to compensate for the temperature-component of the resistance variation of said filamentary metal, whereby said network may respond only to the change in the compositional component of said filamentary metal.

3. In a high temperature metal-treating system in which work is subjected to a gaseous medium having a constituent which gives rise to a constituent-potential towards the work, means for determining said constituent-potential comprising a filamentary ferrous metal so disposed with respect to said work as to be subject to the same temperature and gaseous treating conditions thereof and having a composition such that said constituent-potential with respect thereto is related to said constituent-potential toward said work, said filamentary metal having at least one cross-sectional dimension of a size which produces rapid equalization of said constituent-potential by change in the composition thereof, a network including means for connecting said filamentary metal in one branch thereof, a resistor connected in a second branch thereof, means responsive to the temperature of said gaseous medium for varying the resistance of said resistor to compensate for change in the electrical resistance of said filamentary metal due solely to temperature changes thereof, and means operable by unbalance of said network due to compositional changes in said filamentary metal for indicating the value of said constituent-potential.

4. In a metal-treating system in which ferrous work is subjected to a gaseous medium having at least one constituent which during high temperature treatment of the work is capable of transference between the medium and the work and which gives rise to a constituent-potential therebetween, the combination of a filamentary ferrous metal whose resistance changes with transference in either direction of said constituent between said filamentary metal and said medium, means supporting said filamentary metal for exposure to the same temperature and constituent-transferring conditions as said work for variation of its resistance in one direction on the other concurrently with constituent-transfer between said medium and said work, a balanceable network including means for connecting said filamentary metal therein, variation in the resistance of said filamentary metal producing unbalance of said network in one direction or the other, and means operable in accordance with said unbalance for measurement of said constituent-potential.

5. In a metal-treating system in which ferrous work is subjected to a gaseous medium having at least one constituent which during high temperature treatment of the work is capable of reversible transference between the mdium and the work and which gives rise to a constituent-potential therebetween, the combination of a filamentary ferrous metal whose resistance changes with transference in either direction of said constituent between said filamentary metal and said medium, said filamentary metal having a cross-sectional characteristic for rapid equilibration of said constituent in said filamentary metal with that in said medium by change in the amount of said constituent in either direction of said filamentary metal, means supporting said filamentary metal for exposure to the same temperature and constituent-transferring conditions as said work for variation of its resistance in one direction or the other concurrently with constituent-transfer between said work and said medium, a balanceable network including means for connecting said filamentary metal therein, variation in the resistance of said filamentary metal producing unbalance of said network in one direction or the other, and means operable in accordance with said unbalance for measurement of said constituent-potential.

6. In a nitriding system in which ferrous work is subjected to a nitriding atmosphere at a nitriding temperature having at least one constituent capable at said temperature of transference of nitrogen between the nitriding atmosphere and the work and which gives rise to a nitrogen-potential therebetween to form a case, the combination of a filamentary ferrous metal whose current-varying resistance changes in a corresponding direction with transference in either direction of nitrogen between said filamentary metal and said atmosphere, means supporting said filamentary metal for exposure to the same temperature and nitriding atmosphere as said work for variation of its resistance concurrently with nitrogen-transfer between said atmosphere and said work, means for passing current through said filamentary metal, the magnitude of the current flow varying with change in the resistance of said filamentary metal in one direction or the other due to change in said filamentary metal in one direction or the other of the nitrogen therein, and means operable in accordance with said magnitude of said current flow through said filamentary metal for measurement of the nitrogen-potential between said nitriding atmosphere and said filamentary metal in determination of the nitrogen-content of said case.

7. In a metal-treating system in which ferrous work is subjected to a gaseous medium having at least one constituent which during treatment of the work is capable of reversible transference between the medium and the work and which gives rise to a constituent-potential therebetween to form a case, the combination of a filamentary ferrous metal whose current-varying resistance changes with transference in either direction of said constituent between said filamentary metal and said medium, means supporting said filamentary metal for exposure to the same temperature and constituent-transferring conditions as said work for variation of its resistance concurrently with constituent-transfer between said work and said medium, a balanceable network including means for connecting said filamentary metal therein, a change in the resistance of said filamentary metal producing unbalance of said network, and means responsive to unbalance of said network for varying said constituent-potential in a direction to maintain a predetermined composition of said filamentary metal thereby to control the final composition of said case with reference to said constituent.

8. In a metal-treating system in which ferrous work is subjected to a high temperature carburizing atmosphere having at least one carbon-imparting constituent which during treatment of the work is capable of reversible transference of carbon between the medium and the work and which gives rise to a carbon-potential therebetween to form a case, the combination of an

iron wire of small diameter whose resistance changes with transference in either direction of carbon between said wire and said atmosphere, means supporting said wire for exposure to the same temperature and carbon-transferring conditions as said work for variation of its resistance in one direction or the other concurrently with carbon-transfer between said work and said atmosphere in one direction or the other, a measuring network balanced for a predetermined carbon-content of said wire and unbalanced upon variation of said carbon-content from said predetermined value, and means responsive to unbalance of said network for varying said carbon-potential in a direction to return the carbon-content of said iron wire to said predetermined value thereby to predetermine the final carbon-content of the case of the work being carburized.

9. In a metal-treating system in which work of a ferrous alloy is subjected to a high temperature nitriding atmosphere having at least one constituent which during treatment of the work is capable of transference of nitrogen between the atmosphere and the work and which gives rise to a nitrogen-potential therebetween to form a case, the combination of an iron wire of small diameter whose electrical resistance changes with transference in either direction of nitrogen between said iron wire and said atmosphere, means supporting said iron wire for exposure to the same temperature and nitrogen-transferring conditions as said work for variation of its resistance in one direction or the other concurrently with change of said nitrogen potential of said atmosphere in one direction or the other, a measuring network balanced for a predetermined nitrogen-content of said wire and unbalanced upon variation of said nitrogen-content from said predetermined value, and means responsive to unbalance of said network for varying said nitrogen-potential in a direction to return the nitrogen-content of said iron wire to said predetermined value thereby to control the final nitrogen-content of said case of said work.

10. Means for maintaining the constituent-potential between a constituent of an atmosphere capable of reversible transference between the atmosphere and ferrous metal at high temperature at a predetermined value, comprising a filament of ferrous metal whose electrical resistance at said temperature changes in one direction with change of said constituent-potential in one direction and which changes in the opposite direction with change of said constituent-potential in the opposite direction due to transference of said constituent to vary the net content thereof in said filament in one direction or the other, means supporting said filament in said high-temperature atmosphere and subject to the constituent-potential thereof, a measuring circuit including means for connecting said ferrous filament therein, said filament having a cross-sectional characteristic for rapid attainment upon change of said constituent-potential in either direction of equilibrium between said constituent in said atmosphere and said constituent in said filament, variation in the constituent-content of said ferrous filament producing a resultant change of electrical resistance thereof, and control means reversibly operable in accordance with said change of electrical resistance in one direction or the other to change said constituent-potential of said atmosphere to maintain it at a predetermined value.

11. For a metal-treating system in which work is subjected to a gaseous atmosphere having at least one constituent which during high-temperature treatment of the work is capable of reversible transference between the medium and a ferrous metal and which gives rise to a constituent-potential therebetween, a control system comprising a filament of ferrous metal whose electrical resistance at said high temperature changes in one direction or the other with transference in one direction or the other of said constituent between said filament and said medium to change the net content of said constituent in said filament, means supporting said filament in said high-temperature atmosphere and subject to the constituent-potential thereof, said ferrous filament having a cross-sectional characteristic for rapid attainment, upon change of said constituent-potential in either direction, of equilibrium between said constituent in said atmosphere and said constituent in said ferrous filament, a balanceable network including means for connecting said ferrous filament therein, variation in said electrical resistance of said ferrous filament with change of constituent-content therein in one direction or the other producing by the resultant change of electrical resistance thereof unbalance of said network in one direction or the other, and control means operable in one direction or the other in accordance with the direction of said unbalance for restoring said balance of said network.

12. A control system for metal-treating of the type in which work is subjected to a gaseous atmosphere having at least one constituent which during high-temperature treatment of the work is capable of reversible transference between the medium and a ferrous metal and which gives rise to a constituent-potential therebetween, comprising a filament of ferrous metal whose electrical resistance at said high temperature changes in one direction or the other with transference in one direction or the other of said constituent between said filament and said medium to change the net content of said constituent in said filament, means supporting said filament in said high-temperature atmosphere and subject to the constituent-potential thereof, said ferrous filament having a cross-sectional characteristic for rapid attainment, upon change of said constituent-potential in either direction, of equilibrium between said constituent in said atmosphere and said constituent in said ferrous filament, a balanceable network including means for connnecting said ferrous filament therein, variation of the constituent-content in one direction or the other of said ferrous filament producing by the resultant change of electrical resistance thereof unbalance of said network in one direction or the other, and control means operable in accordance with said unbalance to change said constituent potential of said atmosphere in direction and by an amount to restore balance of said network.

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Certificate of Correction

Patent No. 2,541,857 February 13, 1951

WAYNE L. BESSELMAN ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 4, line 6, for "oms" read *ohms*; column 5, line 43, for "Sqibb" read *Squibb*; line 64, for "disired" read *desired*; column 10, Table II, third column thereof, under the sub-heading "1650° F." for the numeral ".929" read *.939*; same table, fifth column thereof, under the sub-heading "1750° F." for ".853" read *.863*; columns 11 and 12, Table III, seventh column thereof, second line from top, for "0.30–0.50" read *0.30–0.60*; column 13, line 52, for "direction on" read *direction or*; line 65, for "mdium" read *medium*; line 74, after "in", second occurrence, insert *either direction of*; line 75, strike out "either direction"; column 14, line 1, strike out "of";

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of August, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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