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HEAT-TREATED ALLOY STEELS CONTAINING ZIRCONIUM.

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To all whom it may concern:

Be it known that we, FREDERICK M. BECKET and ALEXANDER L. FEILD, citizens of the United States, residing at New York, in the county of New York and State of New York, have invented certain new and useful Improvements in Heat-Treated Alloy Steels Containing Zirconium, of which the following is a specification.

The invention comprises a group of alloy steels, identical in composition with alloy steels which have heretofore been widely used with the exception that the steels included in the invention have a content of zirconium. The invention is restricted to those steels of the said composition which are in the condition resulting from appropriate heat-treatment, said condition being characterized as is well understood in the art by high strength and hardness coupled with sufficient ductility to meet usual engineering requirements. In this condition our novel steels possess mechanical properties of a superior order of merit as compared with steels similarly heat-treated and identical in composition except for the zirconium content.

A large number of heat-treated alloy steels containing zirconium have been made and tested by others. So far as we are aware, these steels have all been of the type described in Technologic paper No. 207 of the Bureau of Standards, in that they contained a high proportion of silicon or nickel, or both. By this is meant that they contained silicon in such quantities as are found in what are technically termed "silicon steels," which are distinguished by having a silicon-content increased to or beyond a point which is more or less critical and lies at about 0.50% Si, for the purpose of obtaining a particular effect; or they contained nickel in the quantities characteristic of what are technically termed "nickel steels," i. e. above about 2.0% Ni. Usually they contained both silicon and nickel in such increased proportion.

Both nickel and silicon belong to that class of elements which when used singly or in combination as alloying additions to steel, do not give rise to the formation of structurally free carbids existing as visibly discrete constituent of the steel. The same class includes cobalt and copper. The steels of our invention do not contain elements of this class in such quantities as are necessary to produce their characteristic alloy steels; we prefer to keep the contents of such elements, if present at all, within the range customary in alloy steels which owe their merit to the presence of alloying elements other than those of the group defined above.

The present invention is distinguished from that covered in our application Serial No. 615,438, filed Jan. 25, 1923, in that the steels to be described and claimed herein contain alloying elements of the class which form structurally free carbids in fully annealed steels containing them in sufficient quantity, viz the elements chromium, manganese, molybdenum, tungsten, and vanadium; and they contain these elements in the proportions in which they normally occur in their characteristic alloy steels; viz in amounts exceeding about 0.4% for chromium, about 0.5% for tungsten, about 0.05% for vanadium, about 0.25% for molybdenum, and about 1.50% for manganese. The phrase "carbid-forming group" as used in certain of the claims is intended to include such elements as those last mentioned and to exclude such elements as nickel, silicon, cobalt and copper, which do not give rise to the formation of structurally free carbids existing as visibly discrete constituents in steel. Whereas it has been generally questioned whether zirconium brings about any improvement when incorporated into the silicon-, nickel-, and silicon-nickel steels reported on by others, we have shown by parallel tests an unmistakable improvement connected with the presence of zirconium in steels included in our invention. The improvement is exhibited in a tendency to maintain the ductility of the steels, as indicated by per cent

elongation and per cent reduction of area, even when these are so treated as to secure great hardness coupled with great strength. This enhancement in properties corresponds, in other words, to an increase in the modulus of rupture without decrease in hardness, and is most marked when the hardness is greater than 300, as measured by the Brinell ball indentation method with a 10-mm. ball and a 3000-kg. load.

The desired effect is brought about in marked degree by the presence in the steel, for instance, of about 0.15% zirconium in the case of a ternary chromium steel containing 0.45% carbon and 0.60% chromium. As a preferred range of zirconium content we would specify from 0.03 to 0.50% zirconium, although we do not consider the present invention to be restricted to any particular range of contained zirconium.

The improvement above described, when brought about by incorporation of zirconium in those alloy steels which are within the scope of the present invention, is quite generally advantageous, but it is of particular advantage in such products as die-blocks, rolls, ball-bearings, cutting tools, case-hardened parts, and, in general, in all products of great hardness which are subject to severe service conditions.

There exist a multiplicity of methods, familiar to those skilled in the art, by which the zirconium may be incorporated in the molten steel. It is preferably added to the steel (for example in the furnace or ladle) in the form of an alloy of zirconium and silicon, but our invention is not limited to the use of zirconium in conjunction with silicon or to its introduction in the form of an alloy. If a silicon-zirconium alloy is used, the ratio of its silicon content to its zirconium content must of course be sufficiently low to permit the desired quantity of zirconium to be added without unduly increasing the silicon content of the steel, that is to say, without bringing the silicon content of the finished steel within the so-called "silicon steel" range.

Table 1 which follows contains under columns I and II the results of tests conducted on two chromium steels tapped from the same electric furnace heat. The steels analyzed 0.45% carbon, 0.62% chromium, 0.19–0.24% silicon, 0.78% manganese, 0.015% phosphorus, and 0.008–0.010% sulphur. They were to all purposes identical in composition and manner of treatment except that the steel described under column I contained 0.16% zirconium, incorporated in the molten steel in the form of an alloy of iron, silicon, and zirconium (ferrosilicon-zirconium). The silicon so added was compensated by an appropriate addition of ferrosilicon to the steels tabulated in column II. Columns I and II contain the results obtained by drawing, at four different temperatures, the steels previously quenched in oil from 850° C.

TABLE 1

	0.45% carbon 0.62% chromium 0.16% zirconium I	0.45% carbon 0.62% chromium II
Drawing temperature	400° C.	400° C.
Per cent elongation	12.0	8.0
Per cent reduction of area	45.9	29.2
Yield point, lbs. sq. in.	178,750	176,200
Ultimate strength, lbs. sq. in.	228,130	215,381
Izod number, ft.-lbs.	9.0	7.3
Brinell hardness	444	444
Drawing temperature	450° C.	450° C.
Per cent elongation	13.0	12.5
Per cent reduction of area	48.7	45.5
Yield point, lbs. sq. in.	172,500	167,500
Ultimate strength, lbs. sq. in.	199,620	189,756
Izod number, ft.-lbs.	18.8	18.4
Brinell hardness	395	402
Drawing temperature	500° C.	500° C.
Per cent elongation	14.0	13.5
Per cent reduction of area	53.9	49.5
Yield point, lbs. sq. in.	147,500	158,750
Ultimate strength, lbs. sq. in.	171,030	177,579
Izod number, ft.-lbs.	30.5	31.2
Brinell hardness	340	364
Drawing temperature	550° C.	550° C.
Per cent elongation	19.0	16.5
Per cent reduction of area	55.3	51.8
Yield point, lbs. sq. in.	133,700	137,500
Ultimate strength, lbs. sq. in.	151,974	159,675
Izod number, ft.-lbs.	41.4	42.3
Brinell hardness	312	336

Table 2 contains under columns I and II the results of tests conducted on two chromium-molybdenum steels tapped from the same electric furnace heat. The steels, which analyzed 0.25% carbon, 0.90% chromium, 0.37% molybdenum, 0.18% silicon, 0.78% manganese, 0.008% phosphorus, and 0.016% sulphur, were quenched from 843° C. in water prior to drawing.

TABLE 2

	0.25% carbon 0.90% chromium 0.37% molybdenum 0.17% zirconium I	0.25% carbon 0.90% chromium 0.37% molybdenum II
Drawing temperature	260° C.	260° C.
Per cent elongation	8.0	5.0
Per cent reduction of area	31.1	17.3
Yield point, lbs. sq. in.	186,140	181,440
Ultimate strength, lbs. sq. in.	229,038	225,816
Brinell hardness	431	444

It should be explained that in these tests, as reported in Tables 1 and 2, the tensile test pieces were machined to exact size before heat-treatment and that they were of standard dimensions (0.505-inch diameter, 2-in. gage length). The test pieces were first maintained for 20 minutes at the temperatures indicated before being quenched. The test pieces, after having been quenched,

were drawn by holding for 20 minutes at the various drawing temperatures. The chromium steel (see Table 1) and the chrome-molybdenum steel (see Table 2) were brought to the normalized and annealed states, respectively, before test pieces were machined therefrom.

The most notable improvement brought about by zirconium occurs, as can be seen, in the lower range of drawing temperatures. The location of this lower range depends, as is well known, upon the composition of the steel and, therefore, cannot be arbitrarily defined. Usually, however, the temperature will lie somewhere between 200° and 600° C.

In the illustrative examples cited above, the steels have been quenched from a high temperature in a liquid cooling medium and subsequently drawn by heating at a lower temperature. Our invention is not considered to be limited, however, to this procedure, but embraces those heat-treating operations which are conducted by cooling in air from a temperature within or above the critical transformation range, provided such air-cooling brings about a material hardening of the steel. In either case, the drawing operation may be omitted when the properties of the steel, as quenched or cooled, are those desired.

Heat-treated steels containing zirconium and containing also certain other alloying elements in normal alloying proportions are described and claimed in our application Ser. No. 615,438, filed January 25, 1923.

Having thus described our invention, what we claim is:

1. Thermally hardened alloy steel containing zirconium, and containing in normal alloying proportion only those alloying elements which belong to the described carbid-forming group.

2. Thermally hardened alloy steel containing zirconium and chromium, the latter in normal alloying proportion, and containing no alloying element of the described non-carbid-forming group in normal alloying proportion.

3. Alloy steel having a Brinell hardness in excess of 300, containing zirconium, and containing in normal alloying proportion only those alloying elements which belong to the described carbid-forming group.

4. Thermally hardened alloy steel containing zirconium in association with an alloying element or elements, the latter in normal proportion, said steel being characterized by substantially higher ductility as indicated by per cent reduction of area than is characteristic of zirconium-free steels of comparable composition, strength, and hardness.

In testimony whereof, we affix our signatures.

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