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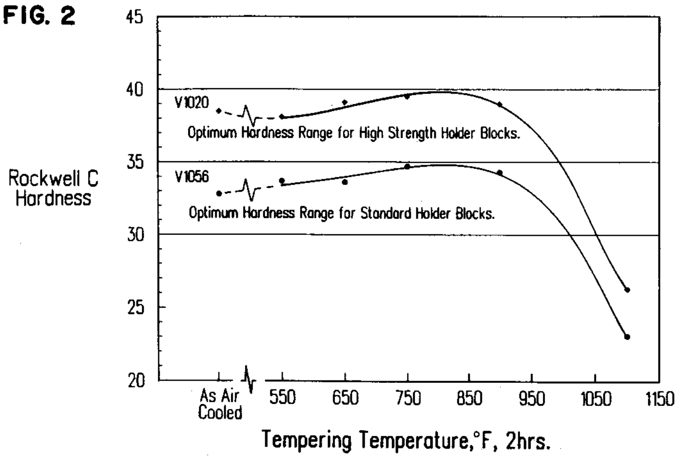
(54) **Martensitic stainless steel article and method for producing the same.**

(57) A martensitic stainless steel having an improved combination of strength, toughness, corrosion resistance and machinability, and particularly adapted for use in the manufacture of holder blocks, frames, backers and similar articles for anchoring molds and dies. The steel has a hardness within the range of 30 to 40 HRC and is consisting of, in weight percent, up to 0.09% carbon, up to 0.09% nitrogen, 0.02 to 0.09% carbon plus nitrogen, up to 4.50% manganes, up to 0.05% phosporus, 0.05 to 0.25% sulfur, up to 1.0% silicon, 1.00 to 4.00% nickel, 11.00 to 14.00% chromium, 0.25 to 1.00% molybdenum, up to 1.00% copper, balance iron and incidental impurities. Articles made from this steel may be austenitized at temperatures within the range of 1500 to 1750 °F for about 1 hour per inch of thickness and either oil quenched or air cooled to achieve a martensitic structure. Thereafter, the article may be tempered or stress-relieved at a temperature between 500 and 850 °F for about 1 hour per inch of thickness with a minimum of 2 hours. After these heat treatments, the article will exhibit a hardness between 30 and 40 HRC, preferably 35 to 40 HRC for higher strength applications, along with a drill machinability rating equal to or greater than 100.

FIG. 2



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The invention relates to a martensitic stainless steel article used for anchoring molds and dies and to a method for producing the same.

DESCRIPTION OF THE PRIOR ART

Molds and dies used to produce parts made from materials such as plastic are anchored in place during operation by frames, holder blocks, backers, and similar articles. These articles are usually made from steel of a composition exhibiting high strength and toughness to withstand the stresses incident to these applications and to provide sufficient service life. The steel must also have good machinability to facilitate manufacture of these articles and must be easily heat-treatable in relatively large section sizes to the necessary hardness limits.

Typical steels used in the manufacture of frames and holder blocks are prehardened within the hardness range of about 30 to 40 Rockwell C (HRC). This eliminates the need for heat-treatment by the user, and avoids the distortion normally encountered in heat-treating of machined articles. The hardness range of 30 to 40 HRC is significant, because the machinability of most steels at hardnesses above 40 HRC is reduced to a level that makes the required machining too expensive for most applications. Although lowering the hardness of the steel improves machinability, at hardnesses below about 30 HRC the steel lacks sufficient mechanical strength for these intended applications.

The low-alloy carbon steels conventionally used for the production of holder blocks, such as the sulfur-bearing modifications of AISI 4140 and AISI 5150, provide an excellent combination of mechanical properties, in combination with good machinability. They, however, lack sufficient corrosion resistance to resist rusting and other forms of corrosion during both service and storage. This corrosive attack reduces the operating safety, efficiency and service life and moreover requires that the holder blocks and frames be covered with a protective coating when they are not in use.

A number of corrosion resistant steels have been evaluated as replacements for the conventional low-alloy carbon steels used in holder block applications. High quality stainless mold steels, such as AISI Type 414, AISI Type 420, and those disclosed in U.S. Patent No. 3,720,545 have been considered; however, they are not widely used for holder block applications because of their cost, properties, and comparatively poor machinability. To overcome the machinability problem, a number of sulfur-bearing modifications of AISI Type 420 and AISI Type 430 have been developed. While these sulfur-bearing steels have relatively good machinability, they are not well suited for this application because their inherent hardening and tempering characteristics make it difficult to produce them in the broad hardness range of 30 to 40 HRC required for holder blocks and especially in the narrower hardness range of 35 to 40 HRC required for high strength holder blocks. In addition, the relatively high austenitizing temperatures used to harden these steels, typically 1825 to 1900 °F, result in increased cost and contribute to considerable distortion of the articles during the hardening heat-treatment. Further, at hardnesses within the range of about 30 to 40 HRC, these stainless steels exhibit a characteristic drop in toughness and corrosion resistance that significantly detracts from their usefulness in these applications.

OBJECTS OF THE INVENTION

It is a primary object of the present invention to provide a martensitic stainless steel article which may be used for holder blocks, frames, backers, and similar articles for anchoring molds and dies, having an improved combination of strength, toughness, corrosion resistance, and machinability.

Another related object of the invention is to provide a method for producing a martensitic stainless steel article having these characteristics by the use of a simple hardening and tempering heat-treatment.

SUMMARY OF THE INVENTION

It has been determined in accordance with the invention that a martensitic stainless steel article having an improved combination of strength, toughness, corrosion resistance, and machinability may be produced by controlling carbon and nitrogen to achieve the desired hardness. Sulfur is controlled in accordance with carbon plus nitrogen to maintain a drill machinability rating equal to or greater than 100 (when compared to a commercial stainless holder block steel). For this purpose, sulfur must be increased with increases in the carbon and nitrogen content. Chromium, and also nickel, are present for maintaining corrosion resistance. Molybdenum is also added for corrosion resistance and specifically to counteract the adverse effects of increased sulfur in this regard. Consequently, molybdenum is increased with increased sulfur contents.

In accordance with the invention, a martensitic stainless steel article, which may be used for holder blocks, frames, backers, and similar articles for anchoring molds and dies, is of a composition within the limits set forth in Table 1.

TABLE I

Composition Ranges of Improved Corrosion Resistant Holder Blocks

Element	Broad	Preferred - Standard Holder Blocks				Preferred - High Strength Holder Blocks			
Carbon	0.09 max	0.06 max	0.06 max	0.06 max	0.06 max	0.09 max	0.09 max	0.09 max	0.09 max
Nitrogen	0.09 max	0.06 max	0.06 max	0.06 max	0.06 max	0.09 max	0.09 max	0.09 max	0.09 max
Carbon plus nitrogen	0.02 to 0.09	0.02 to 0.06	0.02 to 0.06	0.02 to 0.06	0.02 to 0.06	0.06 to 0.09	0.06 to 0.09	0.06 to 0.09	0.06 to 0.09
Manganese	4.50 max	2.00 max	2.00 max	2.00 to 4.50	2.00 to 4.50	2.00 max	2.00 max	2.00 to 4.50	2.00 to 4.50
Phosphorus	0.05 max	0.05 max	0.05 max	0.05 max	0.05 max	0.05 max	0.05 max	0.05 max	0.05 max
Sulfur	0.05 to 0.25	0.05 to 0.10	0.10 to 0.25	0.05 to 0.10	0.10 to 0.25	0.05 to 0.10	0.10 to 0.25	0.05 to 0.10	0.10 to 0.25
Silicon	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max
Nickel	1.00 to 4.00	2.00 to 4.00	2.00 to 4.00	1.00 to 2.00	1.00 to 2.00	2.00 to 4.00	2.00 to 4.00	1.00 to 2.00	1.00 to 2.00
Chromium	11.00 to 14.00	11.00 to 13.00	11.00 to 13.00	11.00 to 13.00	11.00 to 13.00	11.00 to 13.00	11.00 to 13.00	11.00 to 13.00	11.00 to 13.00
Molybdenum	0.25 to 1.00	0.25 to 0.75	0.25 to 0.75	0.25 to 0.75	0.25 to 0.75	0.25 to 0.75	0.25 to 0.75	0.25 to 0.75	0.25 to 0.75
Copper	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max	1.00 max
Iron	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance

The article is characterized by a hardness within the range of 30 to 40 HRC, preferably 35 to 40 HRC for higher strength applications.

In accordance with the method of the invention, steel in accordance with the composition limits set forth in Table I is austenitized at a temperature within the range of 1500 to 1750 ° F for about 1 hour per inch of thickness and either oil quenched or air cooled to achieve a martensitic structure. Thereafter, the article can be tempered or stress-relieved at a temperature between about 500 and 850 ° F for about 1 hour per inch of thickness and for a minimum of 2 hours. After these heat treatments, the articles will exhibit a hardness within the range of 30 to 40 HRC, preferably 35 to 40 HRC for high strength applications, and a drill machinability rating equal to or greater than 100.

Preferably, the article after tempering in addition exhibits a corrosion rate in inches per year of less than 9 when tested in accordance with the procedure disclosed hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the relationship between tempering temperature and hardness for a commercial stainless holder block steel of the composition, in weight percent, 0.32% carbon, 1.33% manganese, 0.32% silicon, 0.097% sulfur, 0.50% nickel, 16.8% chromium, 0.04% molybdenum, 0.034% nitrogen and balance iron and incidental impurities;

Figure 2 is a graph showing the relationship between tempering temperature and hardness for the two indicated holder block steels in accordance with the invention;

Figure 3 is a graph showing the relationship between the hardness of holder block steels in accordance with the invention in the as-hardened condition in relation to the carbon plus nitrogen content thereof;

Figure 4 is a graph showing the relationship between the drill machinability of holder block steels in accordance with the invention with respect to a parameter relating to the hardness and sulfur contents thereof; and

Figure 5 is a series of photographs comparing the corrosion resistance of three holder block steels in accordance with the invention with two holder block steels of compositions outside the scope of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Stainless steel holder blocks are generally made by hot rolling or forging an ingot to slab or billet that is subsequently heat-treated to the desired final hardness and then sawed and machined into blocks of the required shapes and dimensions. Less commonly, the holder blocks are cut and rough machined from fully annealed slabs or billets, heat-treated separately to the desired hardness, and then machined to final shape. The hardness typical of standard holder block applications ranges from about 30 to 35 HRC, whereas that for high strength holder block applications ranges from about 35 to 40 HRC. In order to attain these hardnesses without undue cost or difficulty, it is essential that the steel used in the holder block be readily heat-treatable to the required hardness levels. With stainless steels typical of those now used in corrosion resistant holder blocks, such as that tested to obtain the data presented in Figure 1, the tempering temperatures required to produce hardnesses in the range of about 30 to 40 HRC and especially in the range of about 35 to 40 HRC are quite critical in that slight differences in temperature result in a large difference in hardness. Thus, very close control of the tempering operation is needed with these steels to obtain the hardnesses required for holder block applications. Further, such steels when tempered to hardnesses in the range of about 30 to 40 HRC exhibit relatively low notch toughness and corrosion resistance.

In comparison, with the holder block steels of this invention it is possible to obtain an improved combination of corrosion resistance and toughness and the hardnesses needed for this application with a simple heat-treatment. Figure 2 shows that steel holder blocks produced in accordance with the invention and within the composition limits given in Table I provide the desired hardnesses in both the as-hardened condition and when tempered or stress-relieved over a broad range of temperatures. For example, a steel holder block made from Heat V1056 containing 0.043% carbon plus nitrogen achieves a hardness well within the range needed for standard holder blocks (30 to 35 HRC) in the as-hardened condition and also when tempered or stress relieved at temperatures up to about 850 ° F. Similarly, a holder block made from Heat V1020 with 0.079% carbon plus nitrogen achieves a hardness well within the range 35 to 40 HRC needed for high strength holder blocks in the as-hardened condition and also when tempered or stress relieved over a wide range of temperatures. Also, in contrast to stainless steels of the type now used in corrosion resistant holder blocks, which are normally austenitized from temperatures between about 1825 to 1900 ° F, steel holder blocks produced within the scope of the invention can be austenitized from temperatures as low as about 1550 ° F, which achieves considerable energy savings in heat-treatment.

With respect to the chemical composition of the steels used in the holder blocks of this invention, it is necessary within the composition ranges given in Table I to control their overall composition so that the holder blocks will be substantially fully martensitic in the as-hardened condition. To obtain a substantially fully martensitic structure in the as-hardened condition, it is necessary that the composition of the steels be balanced with respect to the austenite forming elements, such as carbon, nitrogen, nickel, and manganese, and the ferrite forming elements, such as chromium, molybdenum, and silicon, to minimize the formation of delta ferrite. Large amounts of delta ferrite are detrimental in the steel from the standpoint of reducing the hardness and toughness of holder blocks made therefrom.

The hardness of the steels used in the holder blocks of the invention in the as-hardened condition is primarily a function of the carbon plus nitrogen content. To obtain the desired hardnesses within the range of 30 to 40 HRC, it is therefore necessary to control the carbon and nitrogen contents within the ranges indicated in Table I. With a carbon plus nitrogen content that is too low, the holder blocks will not achieve the minimum desired strength and hardness; with a carbon plus nitrogen content that is too high, the holder blocks will exceed the desired maximum hardness and exhibit unacceptable machinability.

Manganese is a desirable element in the steels used in the holder blocks. Manganese imparts hardenability and, in combination with sulfur, is also present for purposes of improving machinability through the formation of manganese sulfide. Also, manganese is an austenite forming element and can be used to partially replace nickel in the steel for composition balance and to thereby reduce steel costs.

Silicon is used in steelmaking for deoxidation and increasing chromium recovery. It also slightly improves corrosion resistance, but is a ferrite forming element and thus increases the amount of costly nickel or manganese needed to obtain a fully martensitic structure.

Nickel is required within the indicated ranges to obtain the desired austenite-ferrite balance and to thereby obtain a substantially fully martensitic structure in the holder blocks. It also improves corrosion resistance; but is a costly element, and for this reason is not desirable above the indicated ranges.

Chromium is essential for corrosion resistance, but above the indicated amounts increases the amount of nickel, manganese, and other austenite forming elements that are required to be present to avoid the formation of delta ferrite and to obtain a substantially fully martensitic structure in the holder blocks.

Molybdenum is an expensive alloying element, but in small amounts and together with chromium has a very beneficial affect on the corrosion resistance of the holder blocks, and a minimum of about 0.25% is necessary for reducing the adverse effects of sulfur on this property. Consequently, molybdenum generally should be increased in the presence of increased sulfur for this purpose.

Sulfur is used for improving machinability, but decreases notch toughness and corrosion resistance. When high toughness and corrosion resistance are required in the holder blocks of the invention, sulfur should be limited to about 0.10%; but when greater machinability is desired, it can be increased to about 0.25% without lowering toughness and corrosion resistance to unacceptable levels. Molybdenum should be increased with increased sulfur to maintain corrosion resistance at the desired level.

Copper is a common residual element in stainless steel melting, and is useful for controlling the austenite-ferrite balance. However, in amounts greater than about 1.0% it can have an undesirable hardening effect during tempering of the holder blocks.

To demonstrate the principles of the invention, a series of experimental holder block steels were made and subjected to a variety of mechanical and corrosion tests. The chemical compositions of the experimental holder block steels and of a commercial stainless holder block steel (Alloy 90-45) included for comparison are given in Table II.

TABLE II

Chemical Composition of Experimental and Commercial Holder Block Steels

Material Code	C	Mn	P	S	Si	Ni	Cr	Mo	N	C+N	Comments
A15770	0.010	0.38	0.029	0.017	0.32	2.86	12.58	0.14	0.022	0.032	Low sulfur
V1009	0.016	0.84	0.020	0.057	0.37	2.74	12.56	0.32	0.032	0.048	
V1033	0.032	0.84	0.020	0.065	0.29	2.75	12.95	0.31	0.018	0.050	
V1087	0.030	0.81	-	0.077	0.34	2.68	12.55	<0.01	0.028	0.058	Very low molybdenum
V1022	0.037	4.06	0.019	0.070	0.32	1.46	12.50	0.32	0.023	0.060	High manganese
V1020	0.054	0.82	0.024	0.060	0.30	2.76	12.72	0.32	0.025	0.079	
V1021	0.024	0.84	0.023	0.120	0.31	2.77	12.59	0.32	0.025	0.049	High sulfur
V1056	0.021	0.82	0.011	0.210	0.31	2.74	12.17	0.29	0.022	0.043	High sulfur
V1055	0.025	4.05	-	0.200	0.32	1.46	12.51	0.33	0.027	0.052	High manganese, high sulfur
90-45	0.320	1.33	0.014	0.097	0.32	0.50	16.80	0.04	0.034	0.354	Commercial stainless holder block

Ingots of the experimental holder block steels were hot worked from a reheating temperature of about 2150°F to bar stock from which samples were taken for metallographic evaluation and testing. Except for those samples used to determine attainable hardness, all the test samples were austenitized at 1550°F, air cooled to room temperature, and then tempered for two hours at 550°F. None of the experimental holder block steels were found to contain any delta ferrite after this heat-treatment. The samples of the commercial stainless holder block steel were received in the prehardened condition at a hardness of 33 HRC. In order to test this material at a higher hardness of 38 HRC, samples of the commercial holder block steel were austenitized at 1850 ° F, oil quenched to room temperature and then tempered for 2 hours at 975 ° F.

Several tests were conducted to compare the advantages of the holder block steels of the invention with those of a commercial stainless holder block steel and to demonstrate the significance of their composition. Tests were conducted to illustrate the effects of steel composition on attainable hardness, notch toughness, tensile strength, machinability, and corrosion resistance.

The attainable hardnesses of the experimental holder block steels in the as-hardened condition are plotted in Figure 3 as a function of their carbon plus nitrogen contents. The specimens for these tests were austenitized for 15 minutes at 1600 ° F and then air cooled to room temperature. Allowing for some normal scatter in the results of the hardness tests, Figure 3 shows that the attainable hardness of the steels used in the holder blocks of the invention has a strong relationship with their carbon plus nitrogen contents. To obtain the hardnesses needed for holder block applications (30 to 40 HRC), Figure 3 shows that the carbon plus nitrogen contents of the holder blocks of the invention must be controlled in a range between about 0.02 to 0.09%. Further, to obtain the hardness typical of standard holder blocks (30 to 35 HRC) and of high strength holder blocks (35 to 40 HRC), the carbon plus nitrogen content of the steels used in the holder blocks of the invention must be controlled from about 0.02 to 0.06% and from about 0.06 to 0.09%, respectively.

The results of the notch toughness and tension tests conducted on the experimental holder block steels and on the commercial stainless holder block steel are given in Table III.

TABLE III

Mechanical Properties of Experimental Holder Block Steels[(a)]

Material Code	Carbon + Nitrogen %	Sulfur %	Hardness HRC	Charpy V-Notch Impact Toughness (Longitudinal) ft-lb	Charpy V-Notch Impact Toughness (Transverse) ft-lb	Tensile Properties (Longitudinal): Tensile Strength ksi	Yield Strength ksi	Elongation (%)	Reduction of Area (%)
V1009	0.048	0.057	32.0	27.0	17.3	150	125	16	58
V1033	0.050	0.065	35.0	30.6	14.6	160	138	16	60
V1022	0.060	0.070	36.5	21.6	17.3	165	134	17	59
V1020	0.079	0.060	38.0	33.0	15.0	172	143	16	59
V1021	0.049	0.120	34.5	21.3	8.3	157	132	15	54
V1056	0.043	0.210	33.0	15.0	6.0	150	127	-	49
V1055	0.052	0.200	35.0	15.0	7.0	160	129	14	49
90-45[(b)]	0.354	0.097	33.0	5.0	3.6	152	129	14	36
90-45[(c)]	0.354	0.097	38.5	5.0	3.0	177	147	15	40

(a) Alloys V1009 through V1055 were austenitized at 1550°F, air cooled to room temperature, and tempered for 2 hours at 550°F.

(b) Commercial prehardened material.

(c) Austenitized at 1850°F, oil quenched to room temperature and Then tempered at 975°F for 2 hours.

These test results show that the notch impact toughness of the steels used in the holder blocks of this invention, as measured in the Charpy V-notch impact test, are clearly superior to those of a commercial stainless steel typically used in this application (Alloy 90-45). The advantage in toughness is particularly great for those experimental steels containing less than about 0.10% sulfur, as can be seen by comparing the notch toughness values of Alloy V1033 (30.6 ft-lb) with those of the commercial stainless holder block steel (5.0 ft-lb). Above sulfur levels of about 0.10%, the impact properties of the steels used in the holder blocks of the invention are still significantly better than that of the commercial stainless holder block steel. For example, the notch toughness of Alloy V1055 with 0.20% sulfur is 15.0 ft-lb in the longitudinal direction; whereas, that of the commercial stainless holder block steel (Alloy 90-45) with 0.09% sulfur is only 5.0 ft-lb.

The tensile properties of the steels used in the holder blocks of this invention are largely a function of their hardness and are at least comparable to those of the commercial stainless holder block steel at the same hardness. About the same mechanical properties and notch toughness are obtained for the higher manganese and lower nickel containing experimental holder block steels (Alloys V1022 and V1055) as for the comparable steels with higher nickel and lower manganese (Alloys V1020 and V1056). Thus, when it is desirable to reduce cost, manganese can be used to replace part of the nickel in the steels used in the holder blocks of this invention.

The results of drill machinability tests conducted on the experimental steels used in the holder blocks of the invention and on a commercial stainless holder block steel are given in Table IV and in Figure 4. The machinability indexes given in this table and figure were obtained by comparing the times required to drill holes of the same size and depth in the experimental steels and in the commercial stainless holder block steel at a hardness of 33.0 HRC and by multiplying the ratios of these times by 100. Indexes greater than 100 indicate that the drill machinability of the test specimen is greater than that of the commercial stainless holder block steel. Because the hardness and sulfur content of these steels are known to influence machinability, a parameter based on these factors [Rockwell C hardness -100 (% S)] was derived and used to compare the drill machinability of the test materials.

TABLE IV

Drill Machinability of Experimental Holder Block Steels[(a)]

Material Code	Carbon + Nitrogen %	Sulfur %	Hardness HRC	Machinability Parameter Hardness -100(%S)	Drill Machinability Index	Comments
A15770	0.032	0.017	31.5	29.8	95	Low sulfur
V1009	0.048	0.057	32.0	26.3	111	
V1033	0.050	0.065	35.0	28.5	103	
V1087	0.058	0.077	34.5	26.8	110	Very low molybdenum
V1022	0.060	0.070	36.5	29.5	97	High Manganese
V1020	0.079	0.060	38.0	32.0	95	
V1021	0.049	0.120	34.5	22.5	113	High sulfur
V1056	0.043	0.210	33.0	12.0	126	High sulfur
V1055	0.052	0.200	35.0	15.0	122	High manganese, high sulfur
90-45	0.320	0.097	33.0	23.3	100	Commercial holder block steel
90-45	0.320	0.097	38.5	28.8	87	Commercial holder block steel

(a) The heat treatment of these alloys is given in Table III.

Analysis of the drill machinability test data using the relationship derived between the above parameter and the machinability index indicates that to provide machinability at least equivalent to that of the commercial stainless holder block steel at a hardness of 33 HRC, the steels used in the holder blocks of this invention must contain at least 0.05% sulfur. Likewise, to provide machinability at least comparable to that of the commercial stainless holder block steel at a hardness of 33 HRC, the holder block steels of the invention at a hardness of 38 HRC must contain at least 0.10% sulfur. These results, in combination with those of the notch toughness tests reported in Table III, indicate that at sulfur levels between about 0.05 and 0.10% the steels used in the holder blocks of the invention afford substantially better notch toughness and machinability superior to that provided by current stainless holder block steels. They also indicate that at sulfur contents between about 0.10 and 0.25%, the steels used in the holder blocks of this invention provide substantially better machinability and notch toughness superior to that of current stainless holder block steels.

Two tests were used to compare the corrosion resistance of the steels used in the holder blocks of this invention to that of a typical commercial stainless holder block steel, the composition of which is given in

Table II. In one test, the weight loss and resulting corrosion rates were determined for specimens immersed for three hours at ambient temperature in a dilute solution of aqua-regia containing 5% nitric acid and 1% hydrochloric acid by volume. This test is described in the literature (E. A. Oldfield, "Corrosion of Cutlery", Corrosion Technology, June, 1958, pp. 187-189) and is particularly useful for comparing the effects of composition and heat treatment on the corrosion resistance of martensitic stainless steels. The term "corrosion rate in inches per year" as used herein refers to the corrosion rate exhibited by an alloy article subjected to this test procedure. These tests were conducted on specimens that were passivated and not passivated prior to testing in a solution of 20% nitric acid containing 3% by weight of potassium chromate at 120°F for 1/2 hour. The other test was a salt spray test in which specimens were exposed for three hours at 90°F to vapors generated from an aqueous solution containing 2.5% by weight of sodium chloride. In this latter test, material performance was ranked visually by estimating the percentage of the surface area that was affected by corrosion. The results of the corrosion tests are summarized in Table V. Photographs of five of the specimens subjected to the salt spray test are shown in Figure 5.

TABLE V

Corrosion Resistance of Experimental Holder Block Steels[a]

Material Code	Carbon + Nitrogen %	Sulfur %	Hardness HRC	Diluted Aqua-Regia Test[b] Passivated	Not Passivated	Salt Spray Test (% Affected Area)	Comments
V1009	0.048	0.057	32.0	4.3	4.2	3	
V1033	0.050	0.065	35.0	4.3	4.3	5	
V1087	0.058	0.077	34.5	-	9.16	40	Very low molybdenum
V1022	0.060	0.060	36.5	6.3	6.3	0	High manganese
V1020	0.079	0.060	38.0	4.3	4.3	0	
V1021	0.049	0.120	34.5	5.5	5.2	8	High sulfur
V1056	0.043	0.210	33.0	3.7	3.3	10	High sulfur
V1055	0.052	0.200	35.0	-	-	5	High manganese, high sulfur
90-45	0.354	0.097	33.0	14.1	13.3	50	Commercial holder block steel

(a) The heat treatment of these alloys is given in Table III.

(b) Corrosion rate in inches/year.

The results of the dilute aqua-regia and the salt spray tests clearly show that the steels used in holder blocks of this invention have substantially better corrosion resistance than a steel typical of that now used in stainless steel holder blocks. This is evidenced by the great difference in the corrosion rates exhibited in the dilute aqua-regia test by Alloys V1033 (4.3 inches/year) and V1021 (5.5 inches/year), whose compositions are within the scope of the invention, and Alloy 90-45 (14.1 inches/year) which is representative of the steels now used in stainless steel holder blocks. The great advantage of the steels used in the holder blocks of this invention is also exhibited in the salt spray test, as can be seen by comparing the percent affected area for these same alloys. The results of the corrosion tests also demonstrate the importance of maintaining the molybdenum content of the steels used in the holder blocks of this invention above about 0.25. In this regard, note, for example, the relatively poor performance of Alloy V1087, which except for a very low molybdenum content had a composition within the scope of the invention, as compared to the good performance of Alloys V1003 and V1009, which contain about 0.32% molybdenum and whose compositions are within the scope of the invention.

The relative corrosion resistance of three of the experimental holder block steels (Alloys V1009, V1020, and V1020) and of two steels (Alloys V1087 and 90-45) outside the scope of the invention is further illustrated in Figure 5. As can be seen, Alloys V1009, V1020, and V1021, having compositions within the scope of the invention, show considerably better corrosion resistance in the salt spray test than do Alloys V1087 and 90-45. The composition of Alloy V1087 is similar to that of Alloys V1009 and V1020, except that it contains less than 0.01% molybdenum. This again demonstrates the importance of maintaining a minimum of about 0.25% molybdenum in the steels used in the holder blocks of this invention. Alloy 90-45 is typical of the steels currently used in stainless steel holder blocks, and its comparatively poor performance again demonstrates that the steels used in the holder blocks of this invention have substantially better corrosion resistance.

The results of the corrosion tests together with those of the mechanical property tests in Table III and of the machinability tests in Table IV clearly show that the corrosion resistant holder block steels of the invention provide a substantially better combination of notch toughness, machinability, and corrosion resistance than afforded by conventional stainless steel holder blocks. Further, the steels used in the holder blocks of the invention have the advantage of being hardenable to the hardnesses needed for this application with a simple heat-treatment.

Claims

1. A martensitic stainless steel article, which may be used for holder blocks, frames, backers, and similar articles for anchoring molds and dies, said article being characterised by having a hardness within the range of 30 to 40 HRC and comprising, in weight percent, up to 0.09% carbon, up to 0.09% nitrogen, 0.02 to 0.09% carbon plus nitrogen, up to 4.50% manganese, up to 0.05% phosphorus, 0.05 to 0.25% sulfur, up to 1.0% silicon, 1.00 to 4.00% nickel, 11.00 to 14.00% chromium, 0.25 to 1.00% molybdenum, up to 1.00% copper, balance iron and incidental impurities.

2. A martensitic stainless steel article according to claim 1 wherein the hardness is 30 to 35 HRC, and in weight percent, the amount of carbon is up to 0.06% the amount of nitrogen is up to 0.06% the amount of carbon plus nitrogen is 0.02% to 0.06%.

3. A martensitic stainless steel article according to claim 1 wherein the hardness is 35 to 40 HRC and the amount, in weight percent of carbon plus nitrogen is 0.06% to 0.09%.

4. A martensitic stainless steel article according to any of claims 1 to 3 wherein in weight percent, the amount of chromium is 11.00 to 13.00% and the amount of molybdenum is 0.25 to 0.75%.

5. A martensitic stainless steel article according to any one of the preceding claims wherein in weight percent, the amount of manganese is up to 2.00% and the amount of nickel is 2.00 to 4.00%.

6. A martensitic stainless steel article according to any one of claims 1 to 4 wherein in weight percent, the amount of manganese is 2.00 to 4.50% and the amount of nickel is 1.00 to 2.00%.

7. A martensitic stainless steel article according to any one of the preceding claims wherein, in weight percent, the amount of sulphur is 0.05 to 0.10%.

8. A martensitic stainless steel article according to any one of claims 1 to 6 wherein, in weight percent, the amount of sulphur is 0.10 to 0.25%.

9. A method for producing a martensitic stainless steel article, which may be used for holder blocks, frames, backers, and similar articles for anchoring molds and dies, said method being characterised by comprising producing said article of an alloy composition consisting essentially of, in weight percent, up to 0.09% carbon, up to 0.09% nitrogen, 0.02 to 0.09% carbon plus nitrogen, up to 4.50% manganese, up to 0.05% phosphorus, 0.05 to 0.25% sulfur, up to 1.0% silicon, 1.00 to 4.00% nickel, 11.00 to 14.00% chromium, 0.25 to 1.00% molybdenum, up to 1.00% copper, balance iron and incidental impurities; austenitizing said article at a temperature of 1500 to 1750°F (833 to 972°C) for about 1 hour per inch of thickness and thereafter air cooling or oil quenching to achieve a martensitic structure and thereafter tempering or stress-relieving said article at a temperature of 500 to 850°F (278 to 472°C) for about 1 hour per inch (2.54 cm) of thickness and for a minimum of 2 hours to achieve a combination of a hardness within the range of 30 to 40 HRC and a drill machinability rating equal to or greater than 100.

10. A method according to claim 9 wherein the amount of carbon plus nitrogen is 0.06 to 0.09 weight percent.

11. A method according to claim 9 wherein, in weight percent, the amount of carbon is up to 0.06%, the amount of nitrogen is up to 0.06% and the amount of carbon plus nitrogen is 0.02 to 0.06%.

12. A method according to any one of claims 9 to 11 wherein, in weight percent, the amount of chromium is 11.00 to 13.00% and the amount of molybdenum is 0.25 to 0.75%.

13. A method according to any one of claims 9 to 12 wherein, in weight percent, the amount of manganese is 2.00 to 4.50% and the amount of nickel is 1.00 to 2.00%.

14. A method according to any one of claims 9 to 12 wherein, in weight percent, the amount of manganese is up to 2.00% and the amount of nickel is 2.00 to 4.00%.

15. The method of any one of claims 9 to 14 wherein said alloy composition has sulfur of 0.05 to 0.10%.

16. The method of any one of claims 9 to 14 wherein said alloy composition has sulfur of 0.10 to 0.25%.

17. The method of any one of claims 9 to 16 wherein said article after said tempering exhibits a corrosion rate in inches per year of less than 9 (22.86 cm).

FIG. I

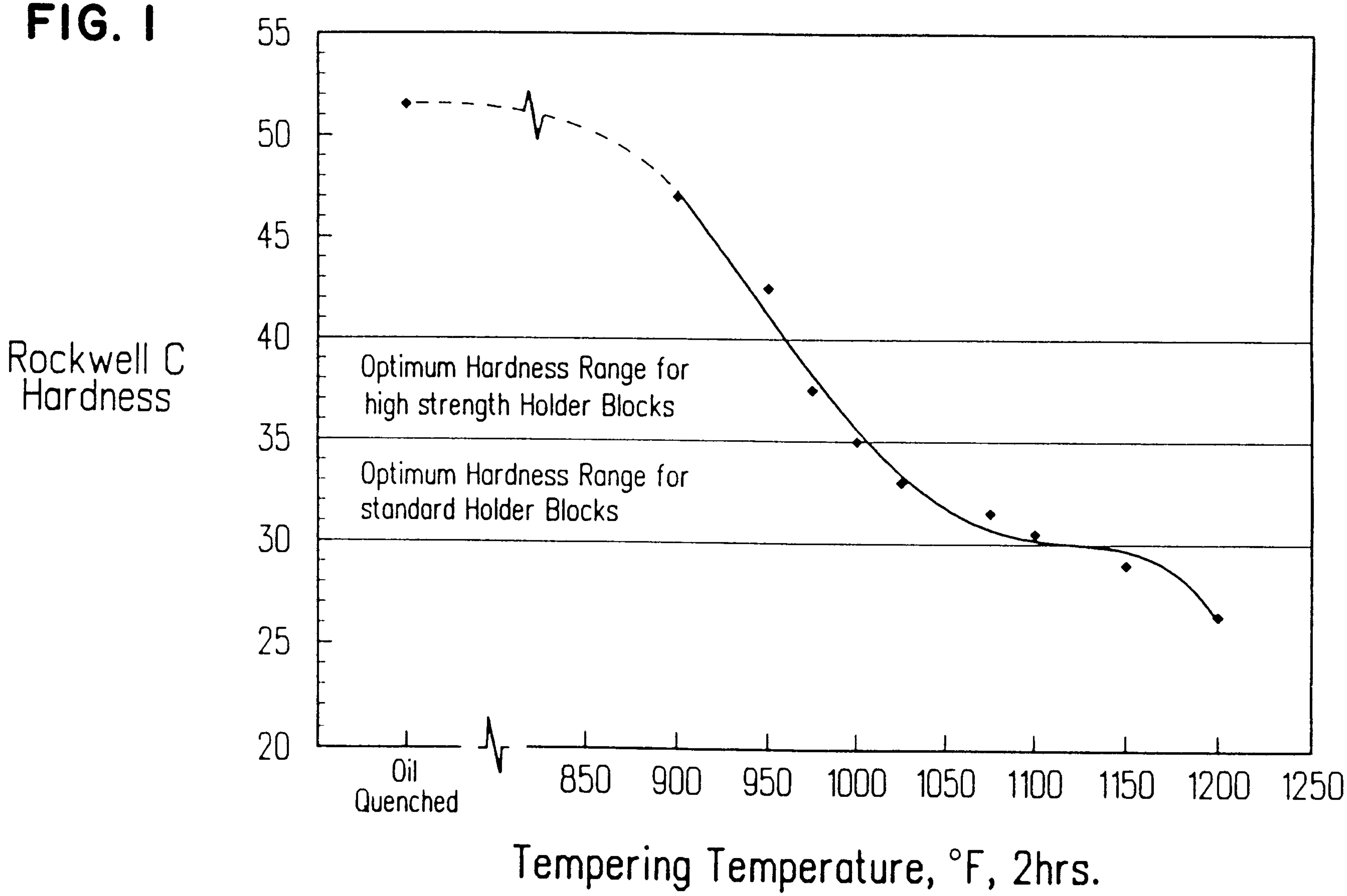

Rockwell C Hardness
55
50
45
40
35
30
25
20
Optimum Hardness Range for high strength Holder Blocks
Optimum Hardness Range for standard Holder Blocks
Oil Quenched
850
900
950
1000
1050
1100
1150
1200
1250
Tempering Temperature, °F, 2hrs.

FIG. 2

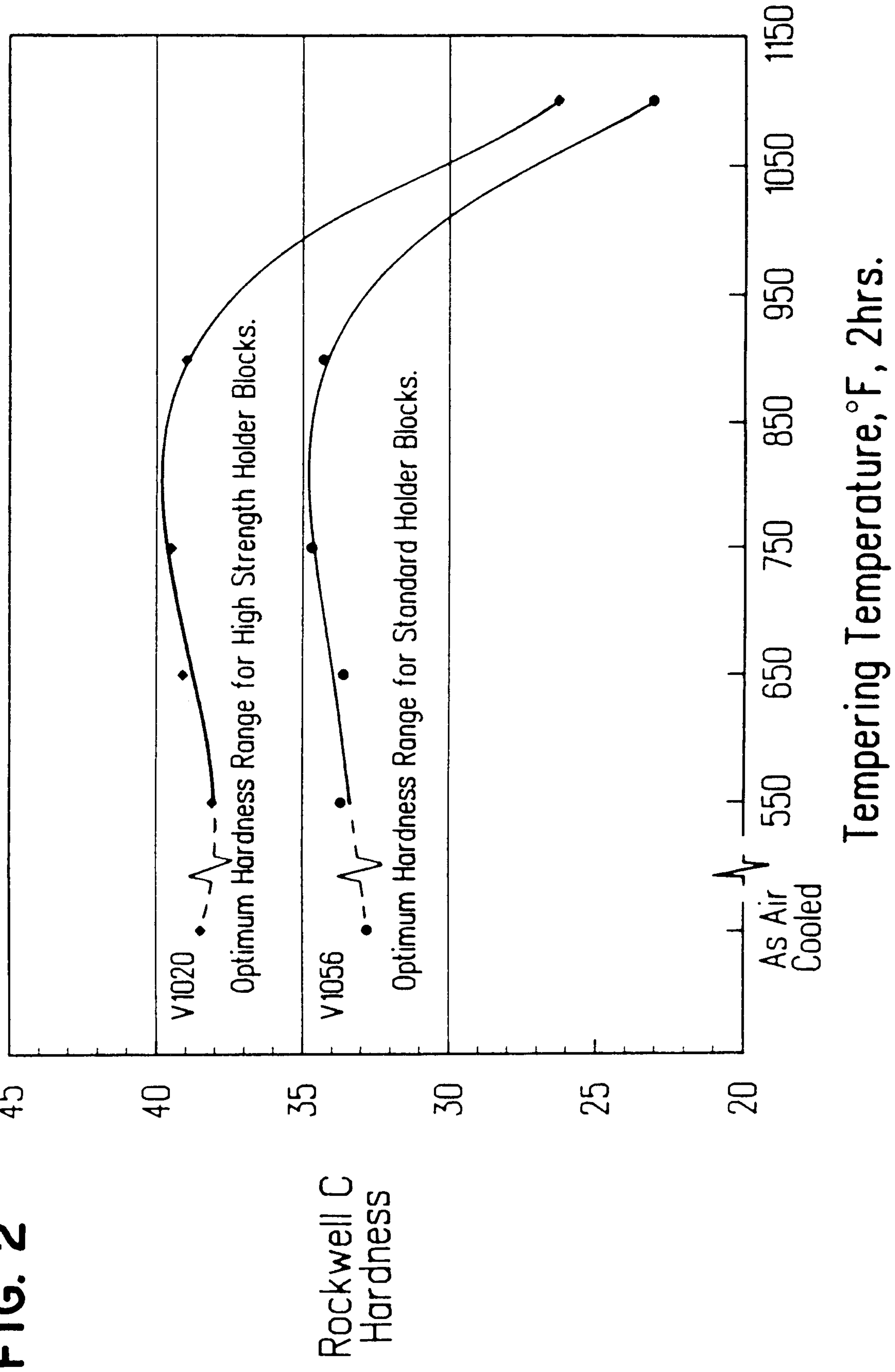

Rockwell C Hardness
45
40
35
30
25
20
V1020
Optimum Hardness Range for High Strength Holder Blocks.
V1056
Optimum Hardness Range for Standard Holder Blocks.
As Air Cooled
550
650
750
850
950
1050
1150
Tempering Temperature,°F, 2hrs.

FIG. 3

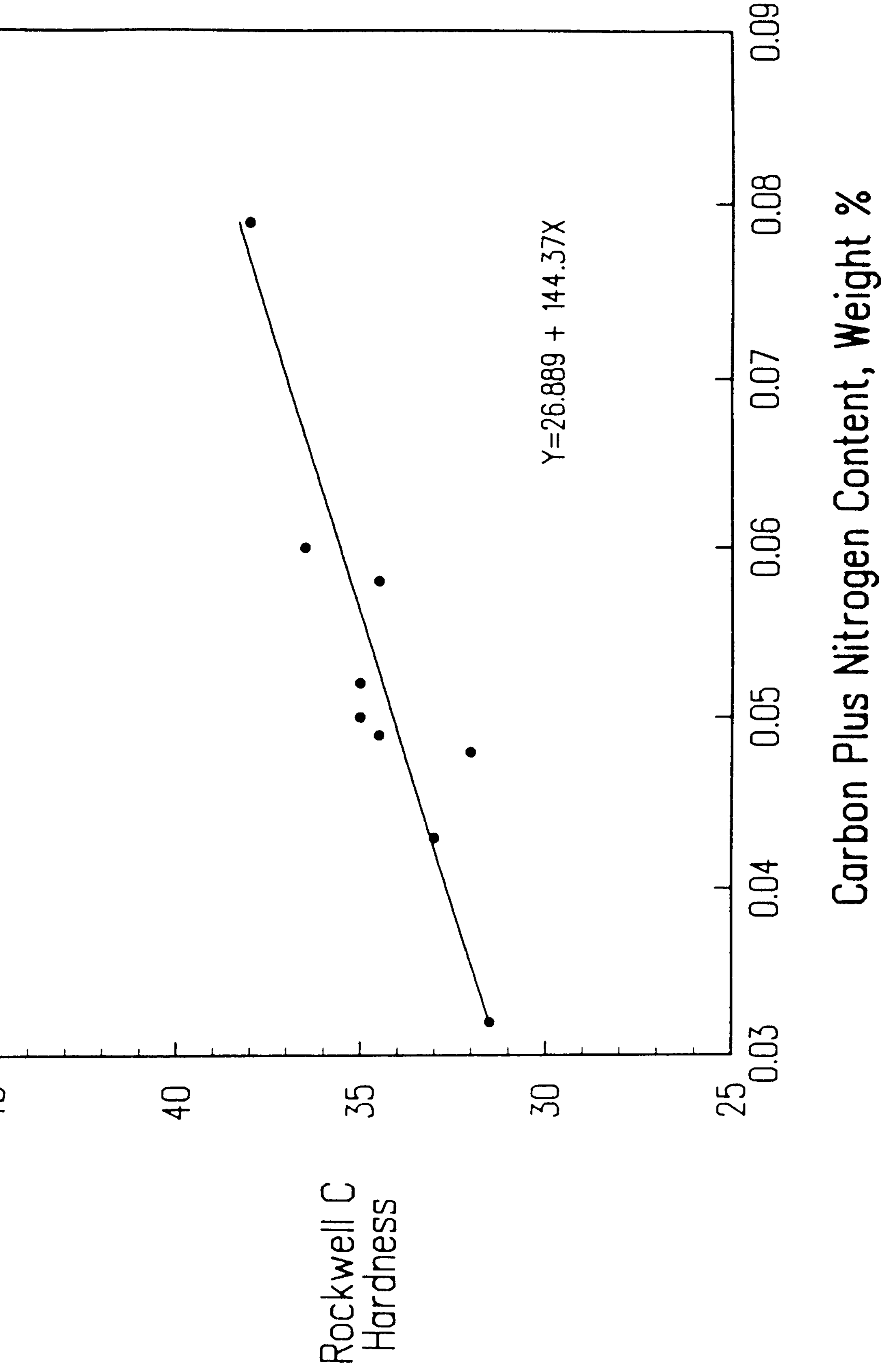

Rockwell C Hardness
45
40
35
30
25
0.03
0.04
0.05
0.06
0.07
0.08
0.09
Y=26.889 + 144.37X
Carbon Plus Nitrogen Content, Weight %

FIG. 4

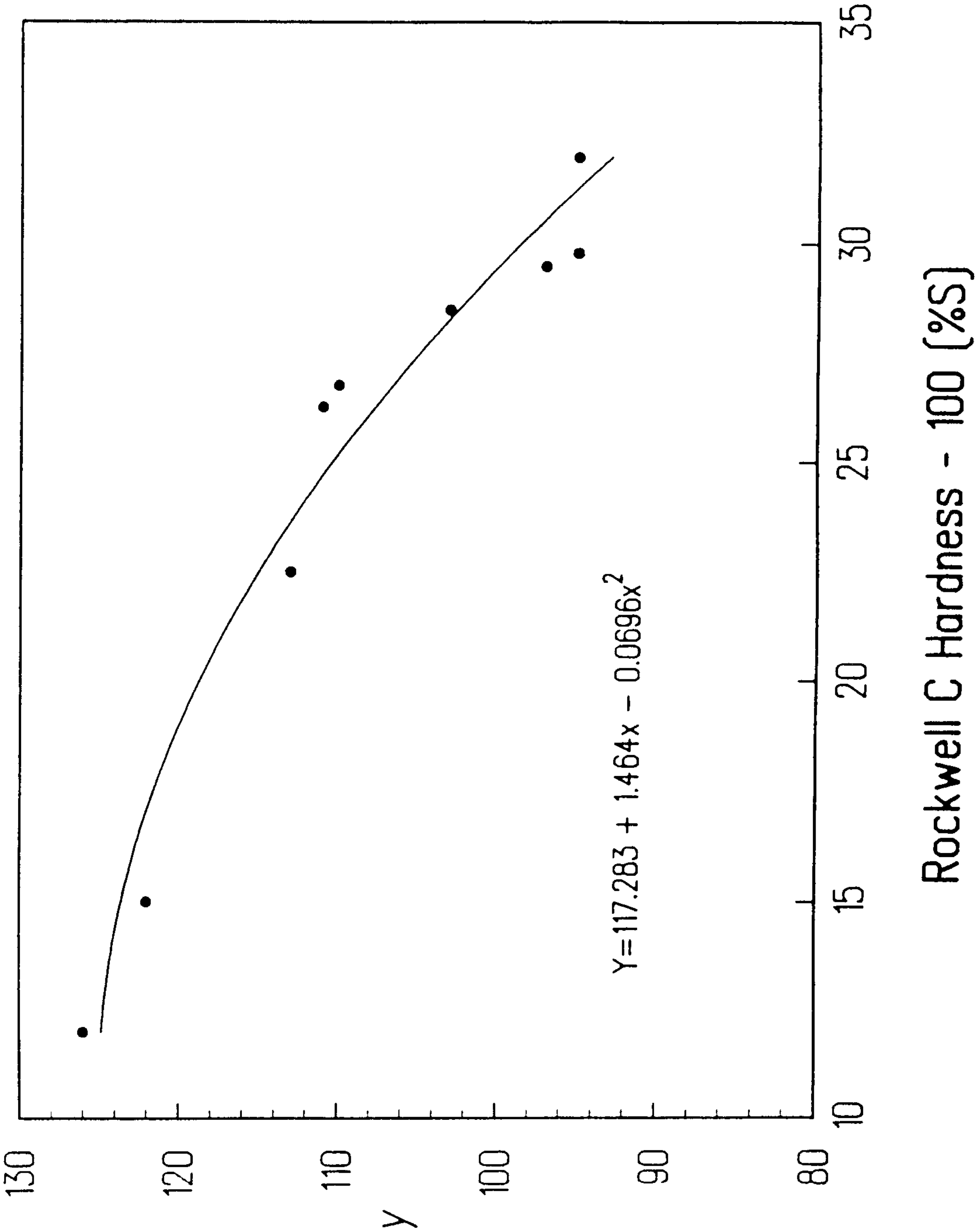
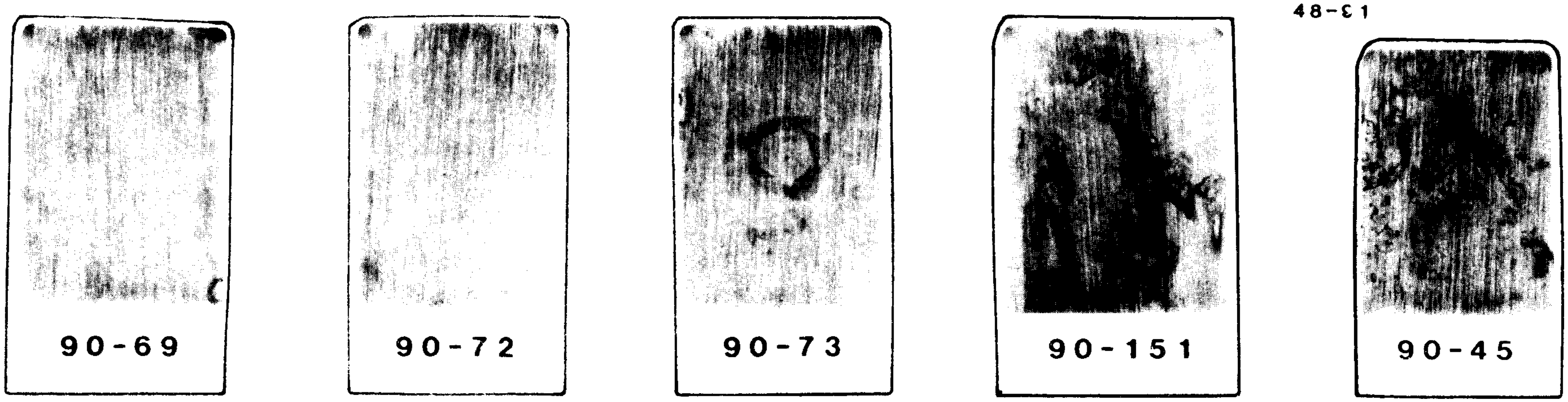

Drill Machinability Index
130
120
110
100
90
80
10
15
20
25
30
35
Y=117.283 + 1.464x − 0.0696x²
Rockwell C Hardness - 100 (%S)

FIG. 5



V1009 (90-69)	V1020 (90-72)	V1021 (90-73)	V1087 (90-151)	90-45
C - 0.016	C - 0.054	C - 0.024	C - 0.030	C - 0.32
Cr - 12.56	Cr - 12.72	Cr - 12.59	Cr - 12.55	Cr - 16.8
Mo - 0.32	Mo - 0.32	Mo - 0.32	Mo - <0.01	Mo - 0.04
Ni - 2.74	Ni - 2.76	Ni - 2.77	Ni - 2.68	Ni - 0.50
S - 0.057	S - 0.06	S - 0.12	S - 0.077	S - 0.097
32 HRC	38 HRC	34.5 HRC	35 HRC	33 HRC

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1473

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 170 598 (UGINE ACIERS) *Claims 1-8; page 2, "Exposé de l'invention", paragraph 3; page 3, l.14-25 and l.31-33; page 9, l.32- page 10,l.7; page 10,l.20-30*	1-4, 7-11,15, 16	C22C38/44
Y	FR-A-1 478 469 (CRUCIBLE STEEL COMPANY OF AMERICA) & BE-A-677 211	1-5,7,8	
Y,D	US-A-3 720 545 (STEVEN ET AL.) * the whole document *	1-5,7,8	
A	EP-A-0 039 052 (TOKYO SHIBAURA DENKI K.K.) * claims 1-11 *	1-5	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02 JULY 1992	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

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