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BLACK OXIDE COATED NITRIDED
STAINLESS STEEL PRODUCTAlexander L. Feild, Baltimore, Md., assignor, by
mesne assignments, to Armco Steel Corpora-
tion, a corporation of OhioNo Drawing. Application February 17, 1945,
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1 Claim. (Cl. 148—31.5)

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This invention relates to stainless steel, more particularly to corrosion-resistant case-hardened stainless steel.

One of the objects of my invention is to provide stainless steel products having a case-hardened finish in combination with outstanding resistance to corrosion.

A further object of my invention is the provision of nitrided stainless steel products having a protective oxide surface film or coating which is thin, elastic and strong.

Other objects in part will be obvious and in part will be pointed out hereinafter.

The invention accordingly consists in the combination of elements and composition of materials, and in the relation of each of the same to one or more of the others as described herein, the scope of the application of which is indicated in the following claim.

As conducive to a clearer understanding of certain features of my invention it may be noted that stainless steel is defined as an alloy steel which includes 10% to 35% chromium, with or without additional percentages of nickel, and with or without supplemental additions of manganese, silicon, cobalt, copper, molybdenum, tungsten, vanadium, columbium, titanium, sulphur, and the like, for special purposes, and a balance which is substantially all iron.

It is a well accepted practice in the prior art to nitride products of stainless steel, often in the machined condition, by subjecting the same to treatment in a nitrogenous medium, such as in ammonia vapor as at temperatures ranging between 930° F. and 1200° F., for increasing wear resistance and surface hardness of the metal. The nitrided stainless steel products have been made to serve a wide variety of uses under corrosive conditions, such as in the form of machine parts which importantly are hard and resist wear.

The nitrided products, however, have not been entirely satisfactory due to a characteristic decrease in corrosion resistance which results from the nitriding treatment, this being true of products fashioned either from straight chromium or chromium-nickel grades of stainless steel. While the decrease in corrosion resistance does not place the steels in the same category of more easily corroded low-alloy carbon steels, the outstanding durability offered by stainless steels nevertheless is considerably diminished by nitriding treatment.

There is clearly an existing incentive for the development of stainless steel articles or prod-

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ucts so as to impart improved corrosion resistance to the same and combine this characteristic with properties bestowed by a nitriding treatment. An important consideration from a practical standpoint which frequently enters is to achieve the property of improved corrosion resistance without effecting substantial changes in dimensions of nitrided stainless steel products which are of approximately finished or final size prior to treatment.

A nitrided stainless steel product surface or surface layer is rich in nitrides of chromium and includes a remarkably small amount of uncombined chromium as compared with non-nitrided stainless steel surfaces. This introduces an unusual problem in treating the nitrided surfaces especially considering that the beneficial properties gained through nitriding are to be maintained without substantial impairment. Among the possibilities of achieving improved corrosion resistance is treatment by chemical action, but such matters as effectiveness, economy and practicability are confronted in the provision of treating chemicals and operating conditions for obtaining the result desired.

I subject nitrided stainless steel products, illustratively wire, bars, rounds, strip and shapes which are more intricate as, for example, indicator needles, valves and valve parts, nozzles, cams, gears, drive wheels and pulleys, washers, bushings and bearings, to the chemical action of fused or molten oxidizing salt of such composition as to give a corrosion-resistant oxide surfacing on the nitrided metal products. The treatment just referred to is effected for a period of time sufficient to develop a corrosion-resistant oxide coating or film on the nitrided products exposed to the salt.

The oxidizing salt which I employ comprises at least one dichromate of the group consisting of sodium dichromate and potassium dichromate. This salt is heated to above fusion temperature, such as to form an immersion bath for the nitrided products, and is maintained in molten condition preferably substantially below its corresponding decomposition temperature range. It is possible, if desired, to resort to increased treating temperatures with potassium dichromate present in the treating salt, for the compound has a relatively high decomposition temperature range as compared with sodium dichromate. By subjecting a nitrided stainless steel product to chemical action of fused salt rich in one or both of the fused dichromates, I achieve on the product a thin, elastic, and strong black oxide surface film

which is instrumental in prolonging resistance of the nitrided metal to corrosive media. A satisfactory film of the character described is obtained by exposing the nitrided metal to dichromate salt treatment usually for from about 5 minutes to approximately 30 minutes time, particularly when sodium dichromate is the predominating constituent of the treating salt. On the other hand, when potassium dichromate as compared with sodium dichromate is included in the treating salt, a less active oxidizing action is exerted on the nitrided stainless steel. In certain instances, therefore, it may be desirable to extend the treating time up to 1 hour depending upon specific composition of the dichromate treating salt. Longer treating periods outside the range specified are not harmful or objectionable, but usually are unnecessary.

The usefulness of the oxide coating which I achieve is readily appreciated. The life of nitrided stainless steel products in corrosive atmospheres or in contact with corrosive media, such as steam, acids, salts, gases, fumes or oils, by virtue of the oxide coating is materially lengthened without substantially impairing hardness or resistance to wear and abrasion of the nitrided case on the steel. Provision of the black oxide coating ordinarily does not appreciably decrease the thickness of the nitrided case, as the thickness of this coating or film usually varies between 0.0001 inch and 0.000005 inch. The thin coating, therefore, has little effect on original overall dimensions of the nitrided products.

As illustrative, I provide a machined and case nitrided stainless steel worm gear and subject the same to cleaning treatment as in a suitable cleaning solution to remove any oil, grease, scale, or the like, which may be present on the nitrided metal surface. I immerse the clean gear in dry condition into a preferred fused oxidizing salt bath which is rich in sodium dichromate, for example to the extent of containing substantially all sodium dichromate, and which is heated to treating temperature within the range of 615° F. to 850° F. and preferably to a temperature between 730° F. and 800° F. The gear is immersed for a period of about 20 minutes while the bath

tively in the form of valve seats, balls, gates and stems where these parts are exposed to the corrosive effect of chemicals, liquids, steam, and the like, especially where the parts are associated with high velocity currents or where steam is conducted through lines at great pressure or at superheated temperatures. The oxide finished nitrided stainless steel valve parts offer resistance to wear and corrosion which permits long life of the valve. In stainless steel articles which serve as bearings, which revolve, rotate, or move back and forth, the oxide nitrided finish assists in preventing a defect known as galling or seizing and gives improved corrosion resistance as compared with uncoated nitrided articles. As a further example, oxide finished nitrided stainless steel cams, gears, gear parts or other moving mechanical devices have the virtue of being highly resistant to wear and corrosion even in locations where grit, dust and dirt together with corrosive gases, fumes or smoke are present. An interesting and still further example of oxide finished nitrided products which I provide are stainless steel heddle wires and similar stainless steel parts which are subjected to continuous buffing and abrading action of cloth threads and are exposed to corrosive acids, dyes and other chemicals carried by these threads.

The value of my corrosion-resistant oxide coated nitrided stainless steel products is reflected to an extent by a series of tests conducted on certain resulting products under various corrosive conditions. In brief, samples of several grades of stainless steel products were subjected to synthetic sea-water, running tap water, and to humid atmospheres for various lengths of time. These samples, consisting of black oxide coated nitrided specimens and uncoated nitrided specimens in pairs formed of like grades of stainless steel were compared at the end of the tests. The tests revealed that the nitrided but uncoated steels were more severely corroded than the oxide finished nitrided specimens. Improvement in corrosion resistance as a result of coating was indicated in each test. The analysis of some of the samples employed in the tests is noted below:

Grade	C	Mn	P	S	Si	Cr	Ni	Ch
12 Chrome.....	0.091	0.12	0.017	0.026	0.16	12.57	0.15	-----
Do.....	0.128	0.34	0.018	0.022	0.23	12.44	0.20	-----
17 Chrome.....	0.064	0.35	0.027	0.023	0.61	17.26	0.53	-----
18-8 Cr-Ni.....	0.051	0.57	0.024	0.022	0.58	18.37	8.76	-----
Do.....	0.064	1.25	0.022	0.015	0.60	18.54	10.92	0.70
25-20 Cr-Ni.....	0.125	1.40	0.011	0.019	0.23	26.44	21.44	-----
17 Chrome.....	0.078	0.44	0.016	0.038	0.43	17.73	0.25	-----
18-8 Cr-Ni.....	0.065	0.59	0.024	0.016	0.47	18.48	8.90	-----
Do.....	0.062	2.16	0.023	0.012	0.55	20.80	12.13	0.86
25-20 Cr-Ni.....	0.129	1.92	0.013	0.053	0.38	27.15	21.61	-----

is maintained at treating temperature and thereafter is removed from the bath, cooled, and then rinsed as in clean water. As a result of the oxidizing treatment the gear has a smooth, continuous black oxide surface film which is adherent, elastic, and strong. In this treated condition the gear is ready for storage, sale or use and is capable of withstanding abrasion and wear with the additional advantage of being adapted to resist corrosion during extended use.

The nitrided and coated stainless steels which I produce are particularly useful in most if not all those commercial fields where nitrided and uncoated stainless steels are desired; illustra-

I have described nitrided stainless steel articles and products of improved corrosion resistance. It will be understood that the invention also pertains to the improvement of carburized or other case hardened stainless steel articles or products. The resultant oxide finished case hardened product also will be understood to form part of my invention.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiments hereinbefore set forth, it is understood that all matter described herein is to be interpreted as illustrative and not as a limitation.

I claim:

A corrosion-resistant case-hardened stainless steel product consisting of a nitrided case-hardened stainless steel portion having a chromium content of about 10% to 35%, and an overlying thin adherent black metal oxide surface film portion of corrosion resistance substantially greater than said nitrided case-hardened stainless steel portion and integrally formed with the nitrided case-hardened stainless steel surface by treatment in a fused salt bath essentially consisting of at least one of the group consisting of sodium dichromate and potassium dichromate.

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