ALLOYS OF NICKEL AND COBALT WITH CHROMIUM.*

By Elwood Haynes.†

The metals nickel and cobalt have always possessed a peculiar interest for the chemist. Like nearly all of the more recently discovered metals, their compounds were known before the metals themselves were discovered. Indeed, it has been known for centuries that certain substances were capable of giving a blue color to glass, and there is but little doubt that this peculiar power was due to some crude compound of cobalt.

About two centuries ago, the ores of cobalt and nickel were encountered in the mining of copper. It was at first supposed that they were ores of the latter metal, but the miners, after vainly striving to smelt the ore, and failing to obtain any copper from it, designated it as "Kupfernick," and from this expression, the word "Nickel" originated.

Attempts were also made to smelt the ores of cobalt, but, as no useful metal resulted, they decided that the goblin, or "Kobold," supposed to inhabit the mines, had placed a ban upon the ore, and thus rendered it incapable of producing valuable metal. From this designation by the German miners, the name "Cobalt" was derived.

It was not until 1751, that Cronsted published the results of an investigation which he had made upon an ore obtained from the mines of Helsingland. This ore yielded a brittle

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metal, and as it occurred most abundantly in "Kupfernickel," he suggested for it the name of Nickel.

A few years later, in 1776, it was discovered that nickel was evidently one of the constituents of a Chinese alloy, known as "Packfong."

The use of nickel in German silver began about the year 1823. It was not, however, until 1857, that Messrs. Deville and Debray, the celebrated French chemists and metallurgists, prepared pure nickel by heating its oxalate in a lime crucible. From the pure metal thus obtained, wires were made, which showed a tensile strength superior to that of wrought iron. The wires also showed considerable toughness, and when polished, presented a bright, silvery appearance, and retained their luster for an indefinite period, under all ordinary atmospheric conditions.

A few years later, the art of electroplating nickel was discovered, and has since received a very wide application. Tons of the double sulphate of nickel and ammonia are used for this purpose every year.

Besides this latter important application of the metal, it is now used in large quantities for the manufacture of nickel steel, which may become a common substance in the making of naval guns, projectiles, armor plate and high-class automobiles.

The history of cobalt is similar to that of nickel, except that the *compounds* of cobalt were used in the arts, instead of the metal, itself. In fact, but little was known of the metal until 1857, when Deville produced the pure metal in practically the same manner that nickel was prepared. It was found that cobalt was even stronger than nickel, possessing a tensile strength of about 65,000 pounds per square inch. Indeed, up to that time, it was the strongest pure metal yet discovered, and it still holds this position, with the possible exception of tantalum.

About the year 1895, I made a number of tentative experiments, relating to the production of alloys of nickel with iron, chromium, and other metals.* The fusions were made in small graphite crucibles, which were heated in a blast furnace of the Fletcher type, operated by natural gas. I had at that time, the advantage of natural gas at a pressure of forty pounds or more per square inch. With a suitably arranged furnace of this character, temperatures ranging up to the fusing point of the most refractory Missouri fire clay, were readily obtained. I succeeded in obtaining, by this means, alloys of nickel and chromium, which contained, however, a considerable amount of carbon and silicon. A small quantity of aluminum was sometimes added to the alloy, in order to improve its quality. By this means, I obtained an alloy of chromium, nickel, and aluminum, which was hard and brittle, but possessed fairly good color and luster. From this alloy a knife blade was formed, which showed fair cutting qualities, and considerable resistance to atmospheric conditions. It was readily soluble in nitric acid, and after long exposures to the atmosphere of a chemical laboratory, it became tarnished, showing a greenish coating on its surface.

Later, I attempted to produce alloys of nickel and chromium with titanium, by means of an electric furnace made from blocks of quick lime. This proved unsatisfactory, but I continued experimenting with the gas furnace, and finally succeeded in producing an alloy of nickel and chromium entirely free from carbon, by heating the pure mixed oxides of the two metals, with powdered aluminum, in a crucible lined with pure oxide of aluminum. The reaction was so violent that most of the metal was thrown from the crucible. A few small pellets were saved, and these showed great malleability, flattening readily under the hammer, without cracking. The alloy possessed a fine color, and when polished,

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*Still earlier Mr. Haynes had done some investigating of alloys in a field which others have proved to be exceedingly fruitful. The subject of his graduating thesis at the Institute in 1881 was "The Effect of Tungsten upon Iron and Steel." By experimenting with very crude appliances, he demonstrated qualities in the tungsten alloys which have made them of immense industrial importance.—Ed.

exhibited a beautiful luster. Larger pellets were soon obtained, and it was found that, when the chromium content much exceeded ten per cent., the alloy showed remarkable resistance to chemical reagents, particularly to nitric acid.

At about the same time, I reduced a mixture of the sesquioxides of cobalt and chromium, with powdered aluminum, and thus obtained minute pellets of an alloy of cobalt and chromium. The little particles thus produced were not much larger than pinheads. They were found to be remarkably hard, and could scarcely be scratched by a file. A few of them were ground off on one side by means of carborundum, and showed a brilliant luster. It occurred to me that the metal might become serviceable for cutting instruments.

A short time after the above experiments were made, I was called actively into the automobile business, and thus compelled to abandon further experiments along this line for some time.

In 1905, I repeated some of the former experiments, with a view to utilizing the alloys of cobalt and nickel with chromium, for ignition points, in connection with gas engines. I was soon able to produce both the alloys of nickel and cobalt in considerable quantity, I ascertained that the nickel-chromium alloy could be worked cold, while the cobalt-chromium alloy must be worked hot in order to obtain any degree of satisfaction.

The first pellets of the cobalt-chromium alloy, weighing from fifteen to thirty grams, were obtained by heating mixtures of aluminum with the oxides of cobalt and chromium, in crucibles lined with the oxide of aluminum. Some of these pellets were heated to redness, and flattened out under the hammer, and while this could be done without cracking the alloy, the metal was found to be very hard, even at red heat.

I soon found that it was impracticable to reduce the alloy in this manner in large quantities. I accordingly purchased a considerable amount of pure cobalt and pure chromium, and had a mixture of nearly equal parts of these metals fused in an electric furnace, the metals being placed in a carbon crucible lined with pure magnesia. The alloy was cast into a small bar, about one-fourth of an inch square, and five or six inches long. This alloy exhibited most of the characteristics of that obtained by reduction with aluminum, but it could not be drawn to any extent under the hammer without cracking. Whether this was due to the high percentage of chromium, or to slight impurities in the metals employed, I am as yet unable to say.

In order to determine what the effect of alloying the cobalt with a smaller percentage of chromium would be, I again had recourse to the gas furnace, and succeeded in melting a mixture containing 75 per cent. cobalt, and 25 per cent. chromium, in a crucible made of a very refractory material, which I compounded for the purpose. Much to my satisfaction, I succeeded in melting this alloy to a perfect fluid and poured it into an ingot mold, which gave me a bar of metal about one-half an inch square, and five or six inches in length. This metal proved to be very sonorous and elastic, and, if some care were used, it could be hammered out into a rough strip.

After a considerable amount of experimenting, with various purifying agents, I finally succeeded in producing a very tough and malleable alloy, which could be hammered out into the thinnest sheet at a bright red heat, without showing signs of cracking. A razor blade was made from a bar of this alloy, and while it did not prove equal to the best steel for this purpose, it has been used hundreds of times for shaving purposes, and, after a year and a half, shows practically no signs of wear, though of course it has been necessary to strop it frequently, in order to keep it in good condition. This bar was made about two years ago, and I am sure that I have since produced metal that would be much more satisfactory for the purpose.

A test of tensile strength and elastic limit of this material was made, with results as follows: elastic limit, 79000 lbs., tensile strength, 96000 lbs., and elongation, 3 per cent. It will be seen from the above that both the elastic limit and tensile strength of this material are superior to those of untreated steel, resembling more nearly those of good nickel steel. The elongation is quite low, but this is to be expected, on account of the great hardness of the alloy, which is equal to that of mild tempered tool-steel. This is a very significant fact, since heretofore it has not been possible, so far as I am aware, to form an alloy of non-ferrous metals, which would show a modulus of elasticity comparable to that of iron and steel. And it is lack of this valuable property in various non-ferrous mixtures, which renders them inferior to iron for many important purposes.

A pocket-knife blade and several table-knife blades were made from this material, and were found to be very satisfactory in every respect. One of these table-knife blades has now been in use for more than two years in the kitchen, where it was used for all sorts of purposes, such as cutting bread, turning griddle cakes, peeling and paring vegetables, and for various other purposes, such as are known only to the culinary art. After this use and abuse, the knife shows not the slightest trace of tarnish, and has held its luster so well that when exposed to the sun, it shows a reflection which dazzles the eyes.

By mixing the alloy with small quantities of other substances, its properties may be modified to a remarkable degree. By this means, I have obtained alloys, or combinations which, while very brittle, would readily scratch quartz crystal.

By reducing the quantity of chromium to some extent, and adding certain other materials, alloys which are practically proof against nitric acid can readily be obtained, which are sufficiently soft and malleable to be worked cold, having a hardness not much greater than that of mild, untempered steel.

Between these two extremes, a great variety of combinations can be made, which are suitable for use for various purposes. For example, I have produced an alloy of sufficient hardness so that when it is formed into a small bar, say one-half an inch wide, one-fourth of an inch thick, and three inches long, and one of the ends shaped for a cold chisel, a 20-penny nail can be cut in two without marring the edge of the chisel in the slightest degree. I have formed another alloy into a small lathe-tool, about one-fourth of an inch square, and three inches long, which showed cutting qualities comparable to high-speed tool steel. In fact, in some respects, especially under high speed and light cuts, it has stood the test for a long time, where high-speed steel failed almost instantly, on account of the intense heat generated. I wish it distinctly understood, however, that I do not recommend this material, as yet, for lathe tools, though it would have a high value for this purpose, if it were not obliged to compete with alloy steels.

An alloy of 75 per cent. cobalt and 25 per cent. chromium, to which small quantities of other metals are added, is not only sufficiently hard for good edge-tools, but is quite tough, and can be bent much beyond its elastic limit without cracking; it resembles in this respect the alloy steels, but, generally speaking, it is much harder. A bar of the alloy, one-fourth of an inch square, can be bent cold at right angles, without showing any signs of cracking.

Chemical Properties.

When the mixture of cobalt and chromium is heated to whiteness in a crucible, the cobalt first commences to fuse, and immediately begins to combine with the chromium, and, if the metals are mixed in the proportion of about three parts, by weight, of cobalt to one of chromium, a eutectic is formed which seems to possess a lower melting point than either cobalt or chromium. This is all the more remarkable because the melting point of pure, carbonless chromium is exceedingly high.

The color of the alloy lies between that of steel and silver, and is especially pleasing in bright light. The alloy is also readily polished, but requires special treatment in order to develop its highest luster.

The most remarkable property of this combination, however, is its resistance to corrosion. It is equalled in this respect only by gold and the metals of the platinum group. It is attacked slowly by dilute hydrochloric acid, and somewhat vigorously by the strong acid, especially when heated. Momentary exposure, however, to either dilute or strong hydrochloric acid, has practically no effect on the metal. Both strong and dilute sulphuric acid attack it very slowly when cold, and not very rapidly even when heated. Nitric acid is totally without action upon it, and a polished piece of the alloy may be boiled in that substance for hours, without affecting the luster of the metal in the slightest degree.

Solutions of the caustic alkalies are also totally without action upon it, even when boiled for hours. The alloy is likewise proof against all atmospheric influences, whether the air be moist or dry, and retains its brilliant luster for months or even years, under severest conditions. Even sulphuretted hydrogen, when present in the atmosphere in large quantity, is totally without action upon it.

Its resistance to culinary operations has already been mentioned.

When the metal is heated in contact with the atmosphere, it retains its color up to a temperature approaching a dull red, or about 500 degrees, Centigrade, when it shows a faint straw color, which deepens as the temperature rises, passing through bronze-yellow, purple, blue, and finally terminating in blue-black.

The alloy does not scale, even when heated to bright orange, and the film of oxide does not seem to increase in thickness after prolonged heating.

It can readily be melted in an open crucible in a gas furnace, with practically no oxidation, so long as a slightly reducing flame is maintained. This is all the more remarkable, on account of its high melting point, which seems to be about 1650 degrees C., for the 25 per cent. alloy. Indeed, the metal has been melted in this manner with a loss of less than one-half of one per cent.

Uses.

The uses for any substance may be limited in several particulars; first, by the limitations of its fitness, second, by the possibility of producing it in proper form, and third, by its cost. This material is particularly suitable for all kinds of small cutting instruments, since it takes an edge comparable to that of tempered steel. It is especially adaptable to the manufacture of pocket knives, on account of the beauty of its color, and the brilliancy of its luster, both of which remain permanent under all circumstances, thus giving the blades a particularly attractive appearance. Knives of this description may be used for cutting fruit, without danger of marring their luster in the slightest degree.

Alloys in certain proportions will also doubtless find a wide use for surgical instruments, since they resist perfectly all sterilizing solutions.

The alloy is perhaps better adapted for table cutlery than anything that has ever yet been produced. We all know too well that a silver plated knife, for example, is ill adapted for cutting meat, and it cannot be sharpened without destroying the plating. Steel knives, on the other hand, while they cut well, require endless labor to keep them in presentable condition, and at best they are unsightly in appearance.

The alloy is also of considerable interest to the chemist and physicist. It is admirably adapted for the manufacture of fine weights for balances, scrapers, spatulas, and other laboratory appliances. To the physicist, it furnishes a material which is at once hard, lustrous and untarnishable, and hence well adapted for the manufacture of fine weights, measuring instruments, and various small tools.

The alloy is also particularly well adapted for the manufacture of standard weights and measures, such as the gram, kilogram, meter, etc., and it is difficult to see in what respect it is inferior for this purpose to the expensive platinum-iridium alloys now in use.

The alloy could readily be made into laboratory vessels, cooking utensils, spoons, forks, etc., and it is limited in this respect only by its cost.

Cost.

Regarding the cost of production and manufacture, I am not at present prepared to make definite statements. I have succeeded, however, not only in obtaining the raw material at lower prices, but have also reduced the cost of production to a considerable degree, so that it is now possible to produce the alloys with as much despatch and precision, as is possible in the production of common alloys.

In conclusion, I wish to add that the chemist seldom receives much credit or pecuniary reward for the discoveries which he is constantly wresting from Nature, and handing down to the engineer and manufacturer. Even the inventor usually receives more credit for his work than the scientist or discoverer, who often furnishes him with the facts and materials which render his invention possible.