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Production Methods Yield 'NEW METALS' For Structural & Engineering Purposes

By JAMES BOYD*

MAN HAS PASSED successively through the stone age, the bronze age, and the steel age, and has now entered an age in which metals play a more vital role than ever before in the world's history. He needs more metals, better metals, and new metals to supply his ever-increasing demands and to meet specifications that are constantly growing more and more rigid.

The phenomenal developments in processes and equipment for both military and industrial use require metals that must withstand heavier stresses, higher temperatures, and unusual conditions of corrosion; in many cases there is a need for metals having such a combination of properties as light weight, strength, and resistance to fatigue.

Most of the chemical elements have been known and isolated for many years, but the true physical properties of certain metals were not recognized until they were prepared substantially free of contaminating impurities. Such metals, formerly regarded as of little industrial importance, when produced in pure form, exhibit properties that have opened up a wide field of usefulness.

WHAT ARE "NEW METALS"?

In a broad sense, the term "new metal" might include a multiplicity of special alloys, as well as a number of rare metals that have been brought into the economic picture because of certain desirable properties that they impart to steel and non-ferrous metals

when added in minor quantities. Most of these rare elements, however, are relatively scarce and so costly that there is little likelihood of their ever being available in large quantities at prices that will permit their wide industrial use as primary structural materials. Molybdenum, vanadium, tungsten, and beryllium are relatively new, but they are marketed chiefly in the form of alloys and sold by the pound rather than on a tonnage basis.

From a practical point of view, therefore, new structural metals may be defined as those that can be derived from abundant sources of raw materials, but have been produced heretofore in very limited quantities for one or more of the following reasons:



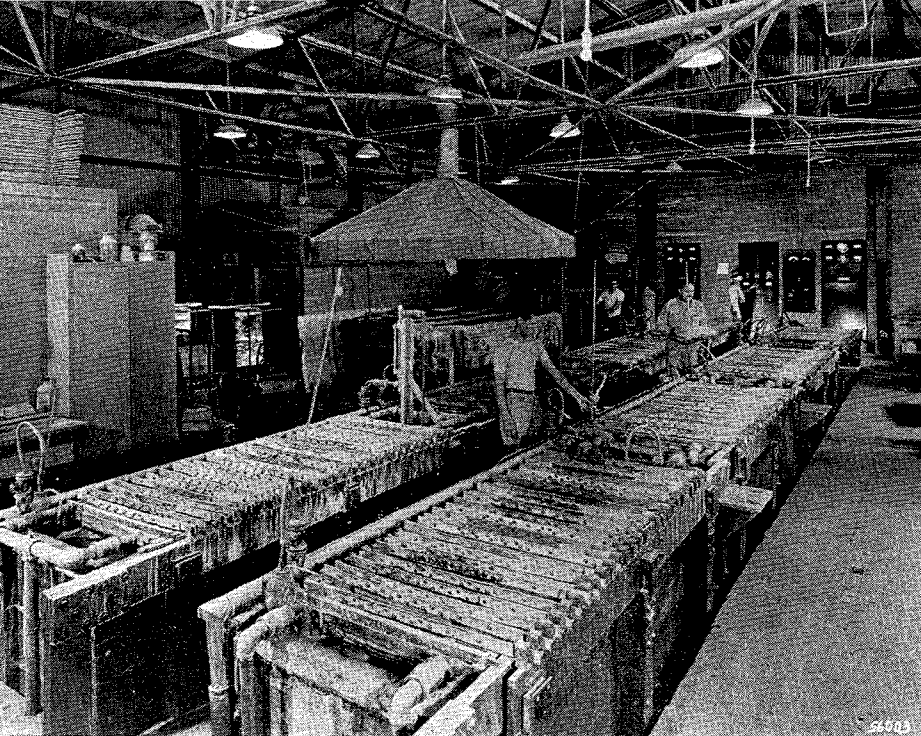
James Boyd recently left his position as dean of the Colorado School of Mines in Golden, Colorado to become Director of the Bureau of Mines in Washington, D. C.

Born in Kanowa, western Australia, in 1904, Dr. Boyd was educated both in the United States and England; received his B.S. degree in engineering and economics from CalTech in 1927, and took his graduate work at the Colorado School of Mines, where he received his M.S. in geophysics in 1932 and his Sc.D. in geology in 1934. He remained at the School of Mines as an instructor, an assistant, and then an associate professor until leaving for service in the army.

Attaining the rank of Colonel during World War II, Boyd served as chief of the Metals and Materials Section, Commodities Branch, Resources Division, Headquarters Services of Supply in 1941-42; and later in other administrative positions.

In 1945, before V.E. Day, Colonel Boyd was sent to Europe to direct the activities of the Production Control Agency under G-4 of the Supreme Headquarters of the Allied Expeditionary Forces and also the Industry Division of the Office of Military Government, the organization which helped to reorganize and re-establish German mines, mills, plants and other industries. Boyd remained in Germany until the summer of 1946, when he returned to the Colorado School of Mines. In recognition of his wartime services, he received the Legion of Merit award, with oak leaf cluster.

* Written in cooperation with the staff of the Metallurgical Branch, U. S. Bureau of Mines.



Cell room of the Bureau of Mines electrolytic manganese pilot plant at Boulder City, Nevada is shown here with the generator controls in the background. (Bureau of Mines Photo)

1. Incomplete knowledge of their properties
2. Technical difficulties in their preparation
3. High cost of production.

Fifty years ago, aluminum and magnesium were new metals so far as their production, price, and industrial uses were concerned, yet these so-called "light weights" are now produced in enormous quantities at a fraction of their former cost, and their value has been firmly established for a wide variety of uses; moreover, the raw materials containing these metals are so plentiful that, as technical knowledge advances, there is little possibility of a dearth of available sources of supply.

The present paper is confined to a discussion of three new metals—manganese, titanium, and zirconium—that are being produced in pure form by processes developed in the Bureau of Mines. The abundant supplies of raw materials available and the unique properties of these metals insure them a permanent and prominent place in the structural field. Their various applications are being determined by cooperation with the metal industry.

ELECTROLYTIC MANGANESE

Manganese, although known and used for many years in the form of ferro-manganese as a scavenger in the manufacture and purification of steel, has been produced in the pure form for only a relatively short time. Electrolytic manganese as developed by the Bureau of Mines may be considered a new metal. Because of its purity, it is extremely valuable in the production of high-quality, low-carbon steels, and as an ingredient of non-ferrous alloys. During the war, it was used as a substitute for nickel in five-cent pieces and it has a promising future as an ingredient of stainless steel.

Although marginal manganiferous ores do not lend

themselves readily to the commercial production of ferromanganese, such ores can be used as raw materials for electrolytic manganese; hence, this development has rendered it feasible to exploit off-grade domestic manganese deposits formerly considered of little or no commercial importance.

The equipment and general scheme for the manufacture of electrolytic manganese from medium-grade or marginal ores can be briefly described as follows:

The plant consists of: (1) a crushing and grinding unit, (2) a roasting or reducing unit, (3) a leaching and purification unit, and (4) an electrolysis unit.

The ore is first crushed and screened to a suitable size, then ground in a ball mill to minus 48-mesh, dried and stored. In the next step, the ground and dried ore is fed to a multiple-hearth muffle furnace, where the manganese dioxide is reduced to the acid-soluble manganese oxide. The reduced ore or calcine is then cooled out of contact with air and conveyed to a storage bin.

The third step consists in leaching the reduced ore with spent electrolyte from the electrolytic cells, with sufficient make-up sulfuric acid added to insure that the manganese is dissolved. The leach is then neutralized with ammonia, and the residue, washed by counter-current decantation until free from soluble salts, is pumped to a tailings pond. The overflow solution from the primary thickener contains metallic impurities, such as arsenic, molybdenum, nickel, and copper, which are precipitated by hydrogen sulfide and removed by filtration. The filtered solution is freed from colloidal impurities by addition of a small quantity of ferrous sulfate solution, which is followed by oxidation, and precipitation of iron and all the remaining contaminants. After standing for several hours, the solution is again filtered and the filtrate is ready for the electrolytic cells.

In the fourth step, the solution of manganese sulfate and ammonium sulfate is fed to lead-lined electrolytic cells having false bottoms which serve as reservoirs for the manganese oxides that form at the anode and spall off periodically. The anodes are of lead containing 1 per cent silver and 0.5 per cent arsenic, and are perforated so as to be 40 per cent void. The cathodes are of stainless steel so treated that the deposit of manganese can be readily stripped off. A frame covered with a canvas diaphragm surrounds the anode, and prevents the acid at the anode from mixing with the solution at the cathode. Direct current for the cells is supplied by rectifiers, and a cathode current density of 45 amperes is maintained with a minimum current efficiency of 60 per cent. The cell potential is 5.3 volts. The cathodes are removed from the cells from time to time, and the deposited manganese is stripped off by flexing or striking the cathodes with a rubber mallet. The cathodes are then cleaned and returned to the cells. An over-all recovery of more than 88 per cent of the manganese from the ore is made.

Mainly through the efforts of the Bureau of Mines, whose publications give detailed descriptions of the various modifications of this process, an electrolytic manganese industry has now definitely been established.

DUCTILE TITANIUM

Titanium has been classed as a rare metal, although its ores are abundant and widely distributed; as a matter of fact, titanium is the fourth most plentiful metallic element in the earth's crust, being exceeded in quantity by only aluminum, iron, and magnesium. Substantial reserves of ilmenite (FeTiO_3), rutile (TiO_2), and other titanium minerals occur in many localities in this country. Certain domestic deposits were drawn upon liberally during the recent war, when imports of ilmenite from India were cut off, and it appears that our native ores will continue to furnish a considerable proportion of the nation's future needs for titanium minerals.

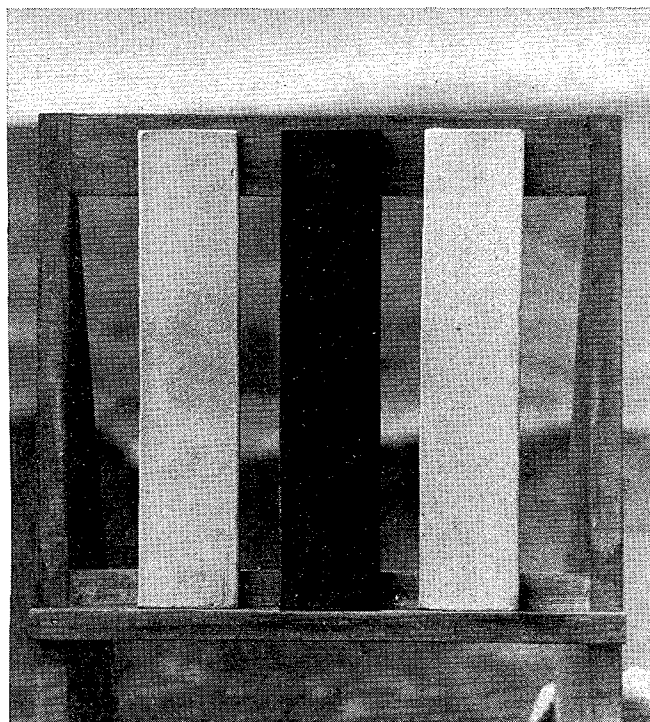
Compounds of titanium have had important industrial applications for many years; the oxide is widely used in the manufacture of an exceptionally white, durable pigment; the chloride is employed in producing smoke screens, in the dyeing industry, and as an intermediate in the manufacture of organic compounds. The

mineral rutile is used for coating welding rods and as a raw material for the manufacture of titanium carbide, a highly satisfactory substance for cutting tools.

Until recently, however, titanium itself was more or less a laboratory curiosity and was considered of little commercial significance. This was due to the difficulty and cost of preparing it sufficiently free from objectionable impurities to bring out its unusual and valuable properties.

Thus far, titanium has not been successfully reduced directly from its oxides, largely because reducing agents, such as carbon, silicon, and aluminum, introduce objectionable impurities into the metal. The Bureau of Mines, however, has developed a method of producing pure ductile titanium by reducing the chloride with metallic magnesium. This process may be briefly described as follows:

Reduction is accomplished in an unlined iron pot fitted with a tight cover and provided with an inlet tube and a well for thermocouple. This pot is heated to 500°C while hydrogen is passed into it to reduce any oxides formed on the interior surfaces. After cooling, clean magnesium ingots are introduced through the inlet tube, and the assembly is again heated to 150°C under reduced pressure to remove absorbed gas. A stream of helium is then passed into the container to provide a neutral atmosphere and the temperature is raised to about 750°C . Liquid titanium chloride is added, at first slowly and then more rapidly as the reaction proceeds, the heat evolved being sufficient to maintain the temperature of the chamber for about two-thirds of the run, after which it is again necessary to apply external heat. A maximum temperature of



Long exposure to the weather has little effect on bars of the rare corrosion-resistant metal, ductile titanium. In contrast to the rusting of the steel bar (center), the titanium bars (left and right) retain their luster. (Bureau of Mines photo)



Demonstrating the unusual tensile strength of ductile titanium, produced in the pilot plant at Boulder City, this smiling laboratory helper is easily supported by a strip of the rare metal about as wide and half as thick as an ordinary book match. The titanium link above the girl's head is 0.131 in. wide and 0.027 in. thick. (Bureau of Mines photo)

determine the purposes for which this new metal seems best adapted.

METALLIC ZIRCONIUM

Zirconium is another new metal appearing on the industrial horizon that offers many advantages in the structural field.

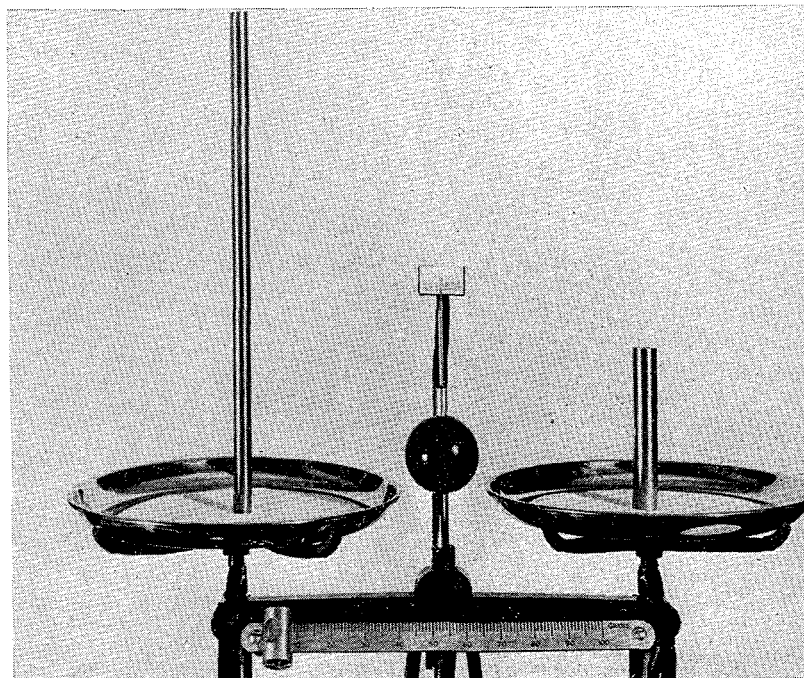
Although this element is not as abundant as titanium, it is more plentiful than copper, zinc, and lead

900° is reached and held for a full half hour after all the titanium chloride has been added. When the reaction chamber cools, the charge is removed, leached with cold hydrochloric acid, the leached metal dried, finely ground, again leached with 10 per cent hydrochloric acid, and finally washed and dried at room temperature. The titanium thus produced is pressed into compacts which, after sintering for 16 hours at 1000° C under a vacuum, are quite ductile and can be readily fabricated.

This process, with certain substantial improvements, is being employed by the Bureau of Mines at its Boulder City Station, Nevada, where a pilot plant having a maximum capacity of about 100 pounds of titanium metal per day is in operation.

The three outstanding properties of titanium that insure its industrial usefulness are: high stress, light weight, and resistance to corrosion. The proportional limit of cold-worked titanium is as high as that of heat-treated steels and aluminum bronze, but its density is only about half as great. In many respects it is similar to stainless steel, yet it has the advantage of a much lower specific gravity, making it an ideal metal for certain vital airplane parts subject to the corrosive action of salt air and sea water.

Substantial quantities of pure ductile titanium are being distributed to various industrial concerns which report to the Bureau the results of tests conducted to



This laboratory balance helps demonstrate the unusual lightness of ductile titanium, one of the "rare" metals produced in the Boulder City pilot plant. Although slightly smaller in diameter, the titanium forged bar in the left balance pan is more than three times as long as the steel forged bar in the right balance pan—yet the two metals balance evenly. (Bureau of Mines photo)

combined, and its ores are widely distributed. The main zirconium mineral available in this country is zircon ($ZrSiO_4$), which is present in substantial quantities in many beach sands. The zircon can be separated from other heavy minerals by standard ore-dressing methods.

Zirconium minerals and compounds have been used for a variety of purposes. Zirconium oxide withstands temperatures as high as 2900° C, or nearly twice the melting point of steel, and hence is finding an increasing market as a refractory; zircon also plays an important role in superdielectrics, heavy-duty porcelain bodies, vitreous enamels, and pottery clays.

As in the case of titanium, the value of metallic zirconium has only recently been recognized, because of limited knowledge of its true properties when produced in relatively pure form. The presence of small quantities of other elements seriously affects these properties.

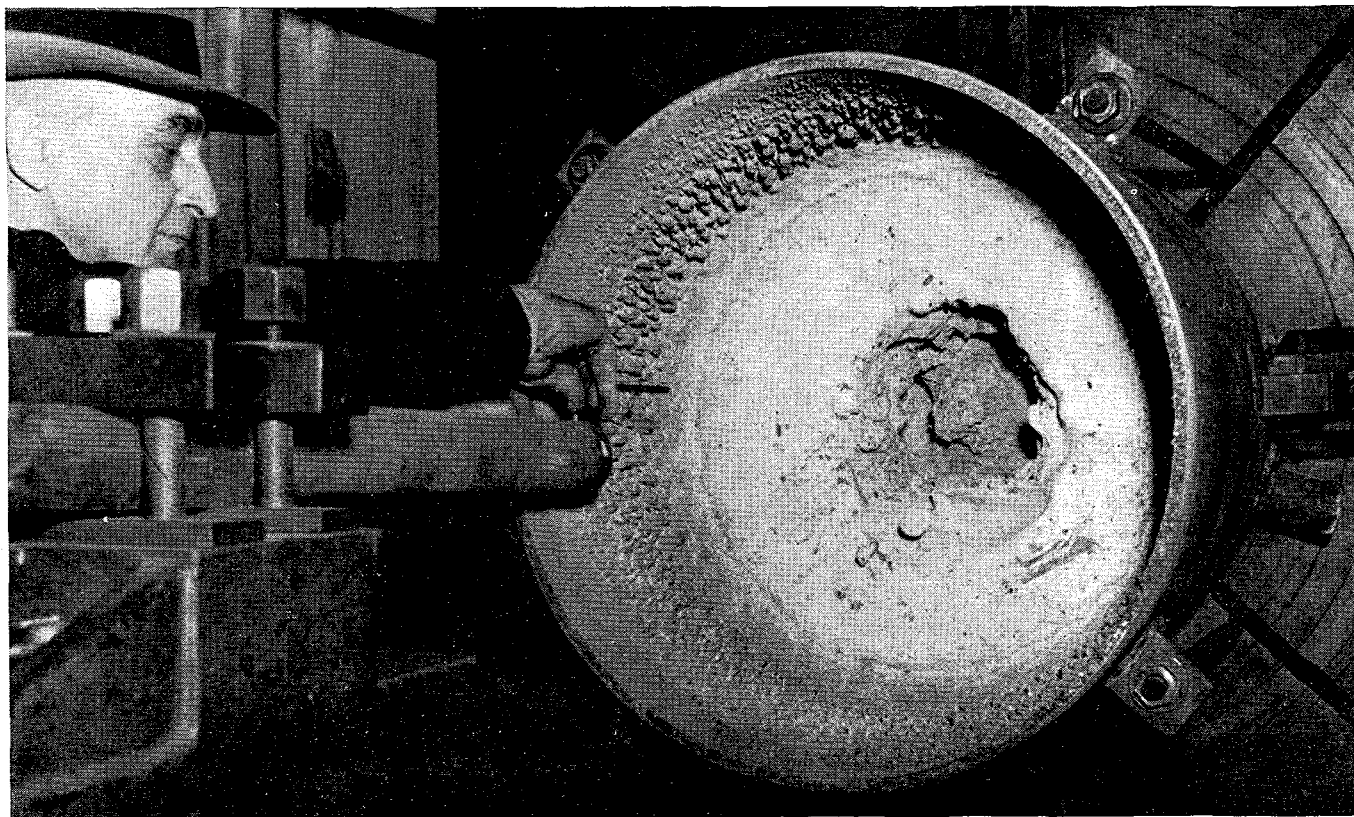
The process for the manufacture of metallic zirconium is similar in many respects to that employed in the production of titanium. Both metals are produced from their own chlorides, but whereas titanium chloride is a liquid that is rather readily obtained in pure form, the chloride of zirconium is a solid that absorbs water from the air, forming oxychloride which gives up its oxygen during the reducing step, seriously contaminating the zirconium metal. The manufacture of zirconium from zircon may be briefly described as follows:

A mixture of zircon and carbon is first reduced to zirconium carbide and silicon carbide in an electric furnace. These carbides are then converted into the corresponding chlorides by passing anhydrous chlorine over or through them at a temperature of 500° C. As the vapor of zirconium chloride is more rapidly con-

denser than that of silicon tetrachloride, it may be collected relatively free from impurities. However, if it becomes contaminated with other metallic chlorides, it can be purified by resubliming in an atmosphere of hydrogen. After separation, the solid purified zirconium chloride is vaporized and the vapor brought into contact with molten magnesium metal and reduced to metallic zirconium. The special furnace employed is operated at a temperature of 850 to 900° C and must be tight but provided with valves to permit evacuation of air and flushing with a neutral gas. Provision must also be made for the automatic release of excessive pressures.

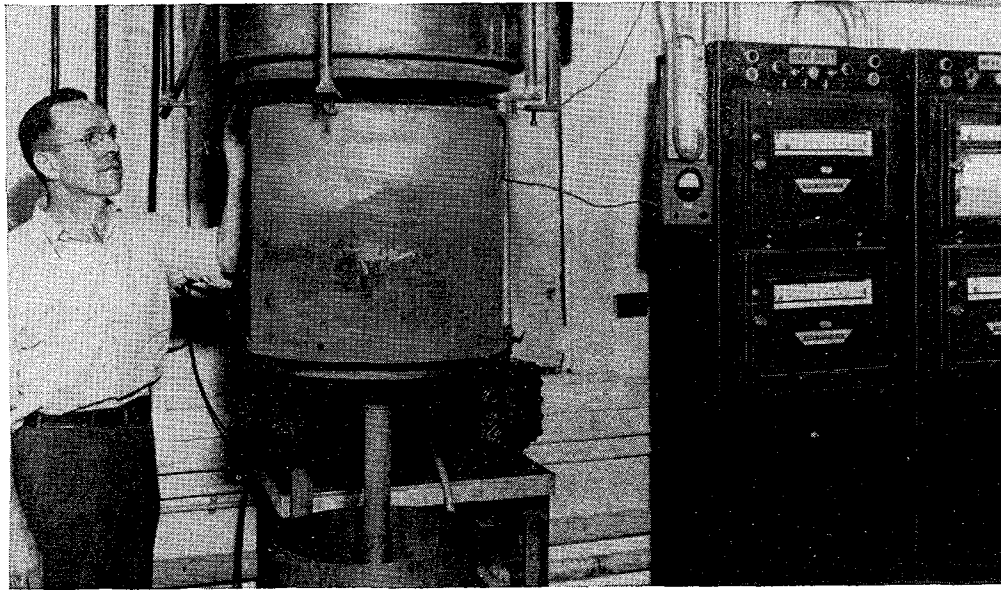
The product obtained consists of a mixture of zirconium metal, magnesium chloride, and residual magnesium. Separation of the zirconium from these other products requires a special step consisting in distilling off the contaminants under a high vacuum at 900° C. The pure zirconium remains in the furnace and, after cooling, is remelted in an atmosphere of helium and cast into ingots for subsequent fabrication. A recent advance in the metallurgy of zirconium has been the development of a successful technique whereby the metal is melted directly in a graphite crucible under vacuum, using a resistance furnace.

Zirconium ingots may be rolled hot or cold; but in the former case, care must be exercised to protect the metal against oxidization. This can be done by enclosing it in a metal sheath, which is subsequently stripped off.



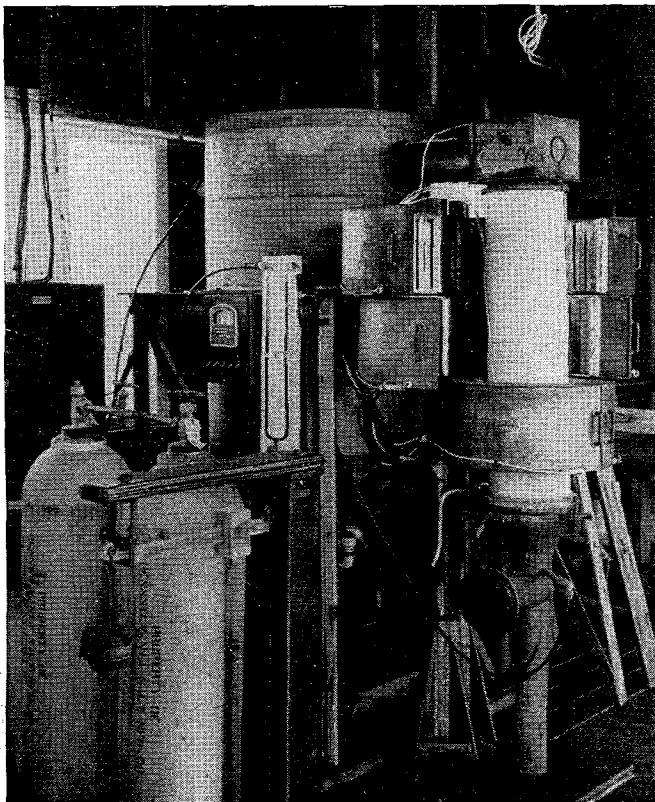
Titanium reduction pot set in lathe ready to cut out charge inside pot. (Bureau of Mines photo)

Vacuum distilling unit showing inverted container from zirconium reduction furnace containing sponge zirconium, excess magnesium and magnesium chloride, and receiver for molten magnesium chloride.



Zirconium is harder than titanium and has greater tensile strength, but is considerably heavier and melts at a higher temperature. One of the most valuable properties of zirconium is its resistance to corrosion by concentrated mineral acids; in this respect it is equal or superior to titanium, a metal that is heavier, less plentiful, and considerably more costly.

Certain military applications of both zirconium and titanium are being developed in cooperation with and with assistance from the armed forces. It is expected that these metals and their alloys will find an important place in our military machine.



CONCLUSION

These "new metals", as the term implies, are still industrial infants. Their properties and structural value have already been demonstrated, but the processes of their manufacture must be improved, simplified, and rendered more economical before such products can be made available at a price insuring production on a tonnage scale.

The three metals discussed in this paper typify the over-all objective of the metallurgical research conducted by the Bureau of Mines. Similar investigations are being carried forward on chromium, cobalt, and other critical metals, as well as on nonmetallic minerals and their products.

The Bureau's established policy is to demonstrate the feasibility of using domestic mineral resources through improved technology and to make available to industry new and better processes and products. The work is usually conducted in several logical steps: first, certain basic principles are established through laboratory research; second, if the results obtained in the first step warrant it, the work is expanded to study factors that can be determined only by larger-scale experiments. This may be the end-point of the investigation, but it is usually necessary to demonstrate the value of the process or product on a semi-commercial scale before industry is willing to adopt it. Therefore, when funds permit, the new development is tested in a pilot plant of sufficient size to prove its commercial practicability. The Bureau then turns over the process or product to industry for commercial exploitation.

Large scale laboratory chlorination unit for production of crude zirconium chloride from zirconium carbide.