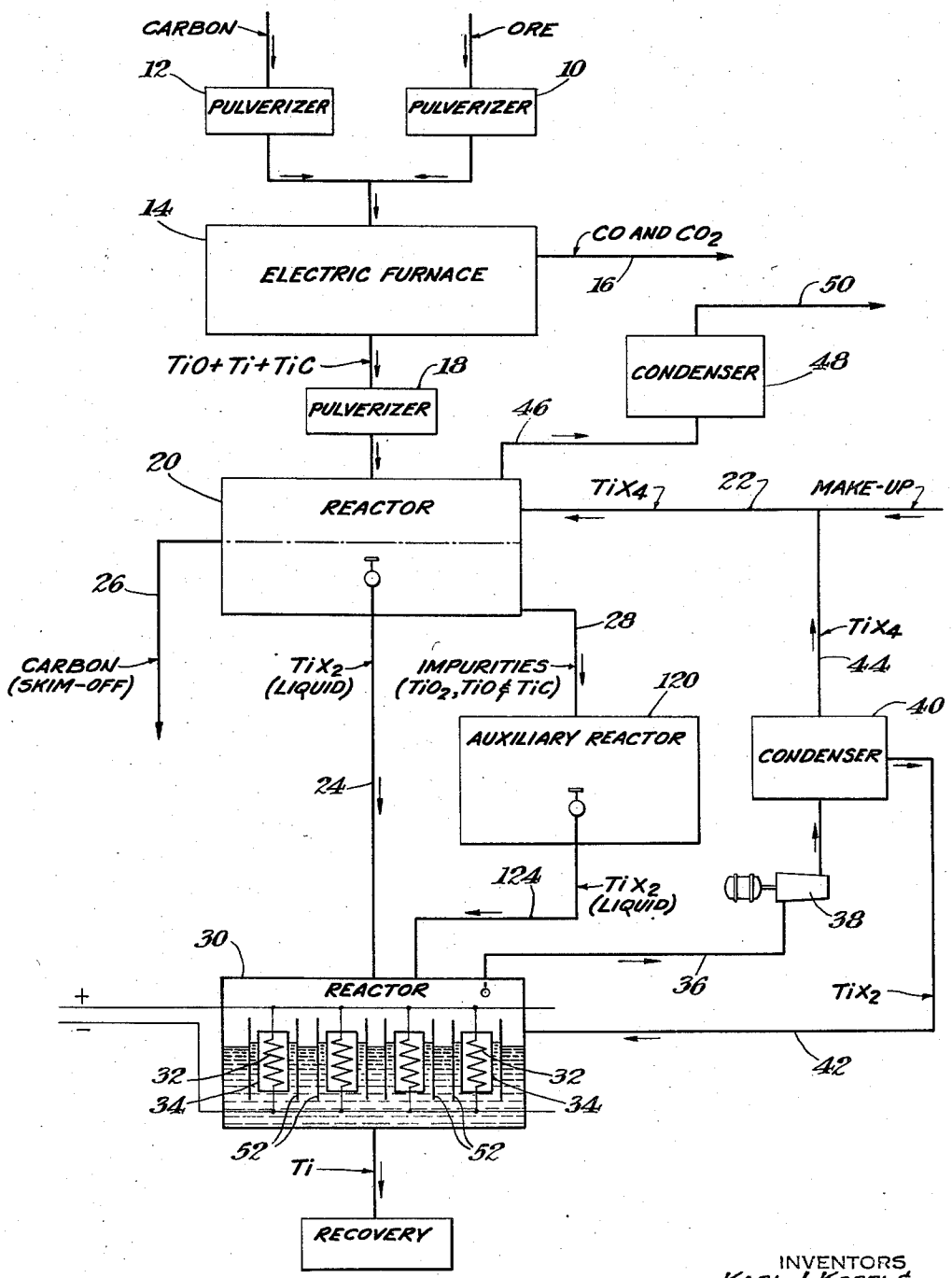
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METHOD OF REFINING METALS

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METHOD OF REFINING METALS

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This invention relates to the production of high melting point metallic elements and has for an object the provision of an improved method or process for producing high-purity refractory metals. More particularly, the invention contemplates the provision of an improved method or process for producing high-purity, high melting point metallic elements by the dissociation of sub-halides of such elements.

This application relates to our copending application Serial Number 543,514, filed October 28, 1955, and entitled "Method of Refining Metals."

Metals such as titanium, zirconium, thorium, tungsten, hafnium, vanadium, molybdenum and uranium, etc., have become important commercial materials in view of the unusual properties which they exhibit. At present, there are several ways of recovering such metals all of which are complicated and expensive. For instance, the procedures now used for the manufacture of titanium are the following:

(1) Reduction of titanium tetrachloride or other titanium tetrahalide with either sodium or magnesium with subsequent elimination of the sodium or magnesium halide which is formed by washing or distillation.

(2) Reduction of titanium oxide with calcium hydride at elevated temperature. This procedure has not been too successful since the product is always heavily contaminated with oxygen.

(3) Thermal dissociation of a titanium tetrahalide on a hot filament under vacuum.

(4) Electrolytic recovery from fused salts.

At the present time, the most widely used commercial method is the reduction of titanium tetrachloride with magnesium or sodium followed by subsequent distillation of the magnesium chloride or sodium chloride by-product in a vacuum. This process, popularly referred to as the Kroll process, is inherently expensive since it produces a titanium halide from a titanous ore and then reduces the halide with another substantially pure metal. In such a process, the necessary expense of the pure secondary metal establishes a very high minimum cost. Also the titanium is formed as a metallic sponge which necessitates further processing to obtain the metal in a useable form.

As indicated, titanium, as well as the other aforementioned metals, have many unusual physical and chemical properties. In order to be workable and generally useful, these metals have to be supplied in an extraordinarily pure form. Small percentages of oxygen, nitrogen, hydrocarbon or carbon embrittle the metal markedly so that it cannot be handled by metal working procedures. Under these conditions, great care is taken to eliminate these undesirable elements from being present while the metal is being formed. While the above noted processes are illustrative of titanium recovery, they are in principal applicable to other metal recovery in pure

elemental form. These processes usually involve the recovery of crystalline metals in the form of extremely small particles or a sponge form of metal. The small particles are inherently unstable and even pyrophoric, readily oxidizing in the presence of air or water, and even react with nitrogen from the air to form nitrides of the metal.

Other difficulties with the treatment and recovery of these metals result from their high melting point. The property of titanium, in the molten state, of acting as a nearly universal solvent presents a major problem in handling the metal in such a state. Almost all of the impurities tolerable in other materials reduce the ductility of the high melting point metals to the degree of being unworkable.

To illustrate our process of producing high purity, high melting point, metallic elements we have hereinafter described our invention with regard to the treatment and recovery of titanium.

In accordance with the present invention, the metal titanium is produced as a relatively high purity product of the little known reaction of titanium monoxide with the titanium halides. Although the reactions of decomposition of sub-halides to metal and higher halides has been known, the possibilities of combined titanium halide reactions have not been appreciated. Through our invention pure ductile titanium is produced in plate or ingot form, rather than in oxidizable crystals or sponge form, and at a cost substantially below that of present day methods. Further, our invention provides a relatively low temperature process which can operate at substantially atmospheric pressure with a minimum of heat input and without the need for hydrogen or other costly reducing materials such as sodium or magnesium. Other objects and advantages of our invention will appear from the following description of one form of embodiment taken in connection with the attached drawing which is a simplified flow diagram of the reaction according to the invention.

In view of the various metals recoverable and variations of equipment which may be used to carry out our process, the flow diagram is to be considered of generally informative nature and illustrative of process steps rather than a limitation as to a specific metal or type of apparatus.

Accordingly, in our method, titanium bearing ores such as rutile, ilmenite and titanite or titanium dioxide-bearing slag obtained as a result of the smelting of titaniferous iron ore, are charged to pulverizer **10**. These ores or slag, even in their purest state, contain iron, silicon and aluminum as regular impurities. Alkaline earth metals, such as calcium, are likewise commonly found in various titania rich ores. We reduce the titanium dioxide of such ores with powdered carbon supplied to pulverizer **12** and produce titanium contaminated with lower oxides including Ti_3O_5, Ti_2O_3 and TiO, and titanium carbide in furnace **14**. The reducing agent fed to pulverizer **12** may be derived from any known carbon source; however, in order to limit contamination of the lower oxides of titanium, we prefer to employ petroleum coke or charcoal. The carbon in the mixture serves primarily to remove the oxygen from the titanium dioxide in the form of carbon monoxide and carbon dioxide, thereby reducing the titanium dioxide to titanium. Some of the carbon may react with the titanium dioxide to form titanium carbide and carbon monoxide and carbon dioxide. To prepare titanium in furnace **14**, we have used a mixture of 80 parts by weight of crushed rutile and 27 parts by weight of crushed petroleum coke, consolidated by pres-

sure to a dense solid. Analysis of the rutile and petroleum coke used by us indicated the following:

Rutile:	Percent
TiO_2	93.20
Fe_2O_3	1.73
SiO_2	2.03
Al_2O_3	0.70
CaO	1.74
P_2O_5	0.60
	100.00
Petroleum coke:	
Volatile matter	8.81
Fixed carbon	89.86
Ash	1.33
	100.00

The furnace **14** may be an electric resistance furnace or it may be of any typical arc, cupola or fluidized design. In the furnace, the titanium dioxide is reduced by carbon by a series of step-wise reactions to produce lower oxides of titanium, elemental titanium, and titanium carbide in accordance with the following chemical equations:

(1) $TiO_2+C \rightarrow TiO+Co$
(becomes favorable about 900–1000° C.)
(2) $TiO_2+2C \rightarrow Ti+2CO$
(becomes favorable about 1500–1600° C.)
(3) $TiO_2+CO \rightarrow TiO+CO_2$ (favorable above 100° C.)
(4) $TiO_2+3C \rightarrow TiC+2CO$
(becomes favorable about 900–1000° C.)
(5) $TiO_2+2TiC \rightarrow 3Ti+2CO$
(becomes favorable about 2000–2100° C.)

A mixed product of TiO and TiC may be obtained in furnace **14** by carrying out the reaction at a temperature of 900–1100° C. In presence of excess carbon, titanium carbide will be the favored product near 1000° C. at atmospheric pressure according to reaction 3. However, it is desired to make the maximum of metal and a minimum of carbide and lower oxides, hence the furnace must be heated to from 1500–2100° C. with the proper carbon ratio to promote reactions 2 and 5. The carbon monoxide and dioxide formed during reduction is driven off under suitable conditions through line **16**.

Products of the furnace other than carbon monoxide and carbon dioxide are cooled to about 700° C. and are in the form of a fused agglomerate containing titanium, titanium carbide and titanium monoxide plus impurities such as small amounts of iron, chromium, vanadium and silicon. The material is ground or pulverized in pulverizer **18** for further handling.

The pulverized titanium-titanium monoxide mixture is then charged to reactor **20**, which is operated under conditions to exclude oxygen, nitrogen and moisture. This reactor is preferably maintained at a temperature of between 600° C. and 8700° C. and at substantially atmospheric pressure. Under the conditions of elevated temperature and controlled atmosphere, the pulverized crude titanium mixture introduced to the reactor is subjected to the action of a higher metal halide vapor entering through line **22** so that an exothermic reaction results. The reaction in reactor **20** is so exothermic in nature that only enough heat to start up is needed from an external source. The temperature within the reactor is controlled by the amount of halide vapor input through line **22**.

We have found that any of the halides which readily combine with titanium may be used to form the halide vapor entering reactor **20** through line **22**. Principally we have formed metallic titanium according to our process using iodine or chlorine, as examples of the halogens, to form the titanium halides. It is obvious that bromine may also be used to form the titanium halide.

For the purposes of explanation, the halide portion of compounds illustrated in the following reactions is noted by the symbol "X" and represents any of the aforementioned elements in the halide group.

The vapor in line **22** is principally titanium tetrahalide (TiX_4) but in some cases may include equilibrium amounts of lower halides and upon reaction with the titanium mixture charged to reactor **20** forms liquid titanium dihalide (TiX_2) which is removed through line **24**.

The titanium higher halides function somewhat in the manner of carriers in accordance with reactions illustrated by the following equations:

(6) $Ti+2TiX_3 \rightarrow 3TiX_2$
(7) $Ti+TiX_4 \rightarrow 2TiX_2$

The titanium oxides and carbide present in the reactor charge that do not react with the higher halides under the aforementioned conditions, remain behind in the reactor as impurities. Depending upon the relative densities of the varied impurities and the particular dihalide used in the process, these impurities will either sink or float. Those that float can be skimmed off the top of the liquid dihalide through line **26**, while those that sink can be removed from the bottom as sludge through line **28**. The dihalide formed can be removed from near the middle of the liquid layer through line **24**.

The impurities of line **28**, comprising mainly titanium carbide and titanium monoxide, can be introduced into an auxiliary reactor **120** for further reaction to produce lower halides of titanium according to the following equations:

(8) $2TiO+3TiX_4 \rightarrow TiO_2+4Tix_3$
(9) $TiC+3TiX_4 \rightarrow C+4TiX_3$

Both of these reactions are favorable at temperatures below about 500° C.; hence such auxiliary reactor should be operated at about 400° C. while the tetrahalide vapor is introduced. This reactor should be operated batchwise so that after charging and reacting the solid titanium carbide and titanium monoxide with the tetrahalide vapor, such reactor is then heated to from 600° C. to 700° C., which is the melting point range of dihalides of titanium. Under these conditions, the trihalides, decompose to dihalides and tetrahalides and the liquid dihalides may thereafter flow through line **124** to reactor **30** to join the flow of liquid dihalides in line **24**. The tetrahalide vapors may remain in the auxiliary reactor to react with a fresh charge of titanium carbide and titanium monoxide at the lower temperatures with additional tetrahalide added as required.

The liquid titanium dihalide (TiX_2) removed from reactor **20** through line **24** is then charged to a second reactor **30** which contains a plurality of electric heating elements generally indicated at **32**. Each heating element is enclosed in a titanium sheath **34** and is maintained at a temperature of from 800° C. to 1150° C. The liquid titanium dihalide pool within reactor **30** is heated by the sheathed heaters to an average temperature of between 600° C. and 800° C. and in this temperature range, the titanium dihalide is thermally decomposed to form elemental or metallic titanium, which deposits on the titanium sheaths or collectors in a high state of purity, and to titanium tetrahalide.

The decomposition of titanium dihalide to yield metallic titanium is according to the following equation:

(10) $2Tix_2 \rightarrow Ti+TiX_4$
(liquid) (solid) (gas)

Any titanium trihalide which may be present is generally unstable and dissociates into titanium dihalide and titanium tetrahalide. The tetrahalide and some of the unreacted dihalide formed during the thermal decomposi-

tion in reactor 30 is in a gaseous state and is removed through line 36 and pumped by pump 38 to condenser 40. In condenser 40, the gaseous mixture is cooled to a point whereby any titanium dihalide is condensed for return to reactor 30 in line 42 while the gaseous titanium tetrahalide is recirculated to line 22 through line 44 and provides substantially all of the tetrahalide requirement of reactor 20.

After the initial starting up of our process, the halide used for reacting with titanium proceeds in continuous circulation between reactors 20 and 30. Only a small amount of tetrahalide is necessary as make-up since the halide circuit is substantially closed with only small amounts of halide loss through the formation of volatile halides of the metallic impurities in the raw material. The volatile halides are removed through line 46 to condenser 48 where the tetrahalide is condensed and returned through line 46 to reactor 20. The volatile halides are then removed from the system through line 50.

Within the reactor 30 there is a continuous deposition and growth of titanium on the heater sheaths 34 whereby they obtain the form of an ingot. Periodically the sheaths are removed and form the pure titanium product after which a new sheath is placed over the heating element and returned to the liquid pool of titanium dihalide.

Around each heater sheath is a refractory thermal barrier 52 which acts to substantially shield the liquid dihalide pool from the higher temperature of the heater while at the same time directs the liquid dihalide in recirculating flow past the sheath for dissociation at the heated sheath temperature.

In some instances the heating elements may also be maintained in the vapor phase over the liquid in reactor 30 as for example where it is found that the particular titanium dihalide used decomposes more rapidly as a vapor.

To illustrate the actual operating conditions of the deposition of highly pure titanium, the following examples are submitted.

Example I

Metallic or elemental titanium was deposited in solid ingot form on a sheathed heater immersed in titanium diiodide (TiI_2).

Vaporous titanium tetraiodide at a temperature in the neighborhood of 380° C. was passed into contact with a bed of crushed slag comprised of lower titanium oxides, titanium, titanium carbide and small amounts of impurities. The crushed slag was maintained at a temperature in the neighborhood of 650° C. The titanium tetraiodide rapidly reacted with the slag to form titanium diiodide, the diiodide forming a liquid pool at a point removed from the slag bed. The liquid titanium diiodide, maintained at a temperature of about 750° C., dissociated on the surface of the heated sheath to form elemental titanium which continually coated on the sheath immersed within the pool and kept at about 950° C., and titanium tetraiodide vapor which was continually withdrawn from the space above the pool.

When the sheath, with the elemental titanium deposited thereon was withdrawn from the pool and weighed, it was found that substantially all of the titanium by weight originally in the slag bed had been deposited on the sheath.

Example II

Metallic or elemental titanium was deposited in solid ingot form on a sheathed heater immersed in titanium dichloride ($TiCl_2$).

Vaporous titanium tetrachloride at a temperature in the neighborhood of 700° C. was passed into contact with a bed of crushed slag comprised of lower titanium oxides, titanium, titanium carbide and small amounts of impurities. The crushed slag was maintained at a temperature in the neighborhood of 725° C. The titanium tetrachloride rapidly reacted with the slag to form titanium dichloride, the dichloride forming a liquid pool at a point removed from the slag bed. The liquid titanium dichloride, maintained at a temperature of about 750° C., dissociated on the surface of the heated sheath to form elemental titanium which continually coated on the sheath immersed within the pool and kept at about 1100° C., and titanium tetrachloride vapor which was continually withdrawn from the space above the pool.

When the sheath, with the elemental titanium deposited thereon was withdrawn from the pool and weighed, it was found that substantially all of the titanium by weight originally in the slag bed had been deposited on the sheath.

Having now described our invention with regard to the production of elemental titanium and having given examples to illustrate modifications of our process, we desire a broad interpretation of the invention as applicable to the production of high melting point metals within the scope of the disclosure herein and the following claims.

We claim:

1. The method of producing a metal selected from the group consisting of titanium, zirconium, hafnium, thorium, tungsten, vanadium, molybdenum and uranium by the disproportionation of an unsaturated halide of the metal, which comprises halogenating a crude mixture of said metal with a saturated halide of said metal, the halogen component of which is selected from the group consisting of chlorine, iodine and bromine, effecting said halogenation in a first reaction zone at substantially atmospheric pressure and at from about 600–870° C. thereby to form an unsaturated halide of said metal and impurities comprising metallic oxides and carbides, withdrawing said impurities from said first reaction zone and introducing them into an auxiliary reaction zone for halogenation therein, effecting said halogenation in said auxiliary reaction zone at substantially atmospheric pressure and at from about 350–500° C. thereby to form additional unsaturated halide of said metal, withdrawing said unsaturated halide as a liquid from said reaction zones and introducing it into a second reaction zone for disproportionation therein to said metal and a saturated halide of said metal, effecting said disproportionation in said second zone at substantially atmospheric pressure and at from about 800–1150° C. in the presence of a body of said metal, depositing disproportionated metal on said body and recirculating the saturated halide formed during disproportionation to said first and auxiliary reaction zones for accomplishing said halogenation therein.

2. The method of producing a metal selected from the group consisting of titanium, zirconium, hafnium, thorium, tungsten, vanadium, molybdenum and uranium by the disproportionation of an unsaturated halide of the metal, which comprises halogenating a crude mixture of said metal with a saturated halide of said metal, the halogen component of which is selected from the group consisting of chlorine, iodine and bromine, effecting said halogenation in a first reaction zone at substantially atmospheric pressure and at from about 600–870° C. thereby to form an unsaturated halide of said metal and impurities comprising metallic oxides and carbides, withdrawing said impurities from said first reaction zone and introducing them into an auxiliary reaction zone for halogenation therein, effecting said halogenation in said auxiliary reaction zone at substantially atmospheric pressure and at from about 350–500° C. thereby to form additional unsaturated halide of said metal, withdrawing said unsaturated halide as a liquid from said reaction zones and introducing it into a second reaction zone for disproportionation therein to said metal and a saturated halide of said metal, effecting said disproportionation in said second zone at substantially atmospheric pressure in the presence of a body of said metal by forming a pool

of said liquid unsaturated halide around said body and maintaining said pool temperature at from about 600–800° C. and said body temperature at from about 800–1150° C., depositing disproportionated metal on said body, and recirculating the saturated halide formed during disproportionation to said first and auxiliary reaction zones for accomplishing said halogenation therein.

3. The method of producing a metal selected from the group consisting of titanium, zirconium, hafnium, thorium, tungsten, vanadium, molybdenum and uranium by the disproportionation of an unsaturated halide of the metal, which comprises halogenating a crude mixture of said metal with a saturated halide of said metal, the halogen component of which is selected from the group consisting of chlorine, iodine and bromine, effecting said halogenation in a first reaction zone at substantially atmospheric pressure and at from about 600–870° C. thereby to form an unsaturated halide of said metal and impurities comprising metallic oxides and carbides, withdrawing said impurities from said first reaction zone and introducing them into an auxiliary reaction zone for halogenation therein, effecting said halogenation in said auxiliary reaction zone at substantially atmospheric pressure and at from about 350–500° C. thereby to form additional unsaturated halide of said metal, withdrawing said unsaturated halide as a liquid from said reaction zones and introducing it into a second reaction zone for disproportionation therein to said metal and a saturated halide of said metal, effecting said disproportionation in said second zone at substantially atmospheric pressure in the presence of a heated body of said metal by forming a pool of said liquid unsaturated halide around said body and maintaining the liquid in said pool at a temperature of from about 600–800° C. by circulation over said body, said body being maintained at a temperature of from about 800–1150° C., depositing disproportionated metal on said body, and recirculating the saturated halide formed during disproportionation to said first and auxiliary reaction zones for accomplishing said halogenation therein.

4. The method of producing titanium by the disproportionation of titanium dihalide, which comprises

halogenating a crude mixture of titanium with titanium tetrahalide, the halogen component of which is selected from the group consisting of chlorine, iodine and bromine, effecting said halogenation in a first reaction zone at substantially atmospheric pressure and at from about 600–870° C. thereby to form titanium dihalide and impurities comprising titanium oxides and carbides, withdrawing said impurities from said reaction zone and introducing them into an auxiliary reaction zone for halogenation therein, effecting said halogenation in said auxiliary reaction zone at substantially atmospheric pressure and at from about 350–500° C. thereby to form additional titanium dihalide, withdrawing said titanium dihalide as a liquid from said reaction zones and introducing it into a second reaction zone for disproportionation therein to titanium and titanium tetrahalide, effecting said disproportionation in said second zone at substantially atmospheric pressure and at from about 800–1150° C. in the presence of a solid body of titanium, depositing disproportionated titanium on said body and recirculating the titanium tetrahalide formed during disproportionation to said first and auxiliary reaction zones for accomplishing said halogenation therein.

References Cited in the file of this patent

UNITED STATES PATENTS

2,670,270	Jordan	Feb. 23, 1954
2,694,652	Loonam	Nov. 16, 1954
2,706,153	Glasser	Apr. 12, 1955
2,720,445	Ruehrwein et al.	Oct. 11, 1955
2,745,735	Byrns	May 15, 1956

FOREIGN PATENTS

722,901	Great Britain	Feb. 2, 1955
723,879	Great Britain	Feb. 16, 1955

OTHER REFERENCES

Mellor: Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 7, pp. 10, 11, 27, 74, 75, 76; publ. 1926.

Barksdale: Titanium, pp. 41, 42; publ. 1949.

Steel, July 24, 1950, pp. 63, 64, 76.