This invention relates to an apparatus for treating materials with chlorine, and more particularly to such an apparatus in which materials can be treated with chlorine at relatively high temperatures.

Many chemical processes involving the use of chlorine gas at relatively high temperatures have been suggested. Chlorine is known to be extremely corrosive for metals under high temperature conditions and prior workers have employed retorts or furnaces of refractory materials or have provided metallic structures with refractory linings so as to prevent contact between metals and chlorine at high temperatures. In accordance with the present invention, I have discovered that under certain conditions nickel can be made extremely resistant to corrosion by chlorine at relatively high temperatures such as retorts, or retorts or furnaces constructed of nickel, having nickel linings, or stationary or removable parts made of nickel, within or associated with the apparatus so as to be contacted by the chlorine, can be employed for processes involving the use of chlorine at such relatively high temperatures.

More specifically, I have discovered that the presence of sulfur or a sulfur chloride in such processes involving the use of chlorine will cause a protective film to be formed upon the surface of the nickel in contact with the reacting materials such that the nickel metal is not corroded by chlorine at temperatures as high as 757°C.

An object of the present invention is, therefore, to provide an improved apparatus for treating materials with chlorine in which nickel having a protective film is employed.

Another object of the invention is to provide as an article of manufacture a metal structure or article consisting essentially of nickel and having formed thereon a protective film preventing corrosion by chlorine.

As stated above, nickel is known to be rapidly corroded by chlorine. However, by forming the protective film referred to upon the nickel, the nickel may be exposed to chlorine at temperatures up to 757°C without any measurable corrosion. The film forms readily at very low temperatures and when once formed will not disappear unless the nickel is heated to temperatures above 757°C. The film is black in color and extremely thin, and shows the qualitative presence of sulfur and chlorine as well as nickel, although it has not thus far been possible to determine the exact composition of the film. The formation of the film apparently requires the presence of a sulfur chloride but is apparently independent of constituents other than sulfur and chlorine.

It is, of course, apparent that it is not necessary to introduce a sulfur chloride into the reaction chamber in which the film is formed, as the sulfur chloride may be formed in situ. Free sulfur and many sulfur compounds will react with chlorine to form sulfur chlorides. Thus the presence of free sulfur or such compounds as iron sulfide or other sulfides, found in many ores, provides for the formation of such film.

The film is extremely thin and resistant to abrasion, as furnaces provided with nickel rabble arms scraping ores of relatively abrasive nature over nickel surfaces have been employed for extended periods of time without showing any more than the wear which would be normally expected from such operations in the absence of corrosive gases. When once formed, the film is persistent, as the sulfur or chlorine, or both, can be removed from contact with nickel and the furnace used for other purposes for considerable lengths of time at temperatures below 757°C. Without destruction of said film. It is, therefore, entirely possible to intermittently introduce sulfur, sulfur-containing compounds or a sulfur chloride into such a furnace to form said film and thus employ the furnace for continued treatment with chlorine in the absence of sulfur. The present invention has thus far found its chief utility in the chlorination of ores to remove volatile compounds of metals, chlorine and sulfur, as disclosed in Patents No. 1,834,622; 1,923,094; 1,858,272 and 1,863,599. A structure of a furnace suitable for carrying out the processes of the above patents is disclosed in my Patent No. 2,116,725. Such a furnace includes many moving parts and also the provision of external heating means for supplying heat through the walls of the treating chamber to the materials being treated in order to maintain the necessary or desirable treating temperature. It was, therefore, desirable to construct such a furnace of metal, but no suitable metal was known prior to the present invention which could be commercially used. The film has been formed and maintained in furnace work with titanium, vanadium, tungsten and aluminum bearing ores, indicating that the formation of film is independent of constituents other than the chlorinating gases containing chlorine and a sulfur chloride. It is evident that the present invention is not limited to the treatment of ores but may be employed in any process involving the
treatment of materials with chlorine and in which the presence of sulfur is not objectionable. It has also been found that the film will be formed upon nickel alloys, the major portion of which consists of nickel. Thus nickel alloys can be employed under certain conditions, although the presence of substantial amounts of other metals in the alloy somewhat reduces the temperature of operation. For example, a 90% nickel-10% chromium alloy has been found satisfactory up to a temperature of 525° to 650° C., the film disappearing at only a slightly lower temperature than with pure nickel. It will be seen that I have provided an apparatus by which materials can be treated with chlorine at relatively high temperatures in metallic reaction chambers without corrosion, thus providing for treating chambers having high mechanical strength and the efficient application of external heat to the reaction.

It is apparent that articles of manufacture, for example, pipes, valves, machine parts, or sheets of nickel or metals containing a major portion of nickel may have one or more surfaces provided with the protective film of the present invention and may be sold or used for purposes in which the metal is subjected to corrosion by chlorine. After once being formed, the film is resistant to abrasion and persistent in the presence of chlorine as well as in the presence of chlorine and sulfur chloride. Furthermore, the film has been found to withstand weathering for extended periods of time upon articles exposed in the open. The film may be formed upon such articles by treating them in a chamber containing chlorine and sulfur chloride or, in the case of hollow articles such as pipes or reaction chambers, by circulating chlorine and sulfur chloride through or introducing the same thereto. Also, a layer of nickel or a nickel alloy consisting essentially of nickel may be plated or otherwise formed upon a base metal and the film formed upon the surface of the layer.

This application is a continuation in part of my co-pending application serial No. 126,158, filed March 29, 1933.

While I have disclosed the preferred embodiments of my invention, it is to be understood that the details thereof may be varied within the scope of the following claims.

I claim:
1. As an article of manufacture, a structure having a surface of metal containing a major portion of nickel, said surface being provided with an integral protective film consisting of said metal of said surface, chlorine, and sulfur.
2. As an article of manufacture, a nickel metal structure having a nickel surface provided with an integral protective film consisting of said nickel, chlorine, and sulfur.
3. As an article of manufacture, a metal structure having a surface layer of metal containing a major portion of nickel, said layer having its exposed surface provided with an integral protective film consisting of said metal of said layer, chlorine, and sulfur.

LESLE G. JENNESS.