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Processes occurring during the manufacture of form based on magnesite oxide and casting titanium products

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Abstract. In this work investigate the chemical processes occurring during the manufacture of magnesium oxide-based mold and casting titanium products to prevent the formation of alpha case. When molten titanium is poured into the mold due to low thermal conductivity the mold is heated unevenly. The resulting carbon dioxide and active metal compounds migrate to the more heated regions adjacent to the surface of the casting. The increased concentration on the surface of the O, Si, Ca, Na forms promotes the reactions to form active metal titanates.

1. Introduction
Titanium has a high corrosion resistance and belongs to reactive metals due to the stable passive TiO\textsubscript{2} film on titanium surface, which is bound up with the base metal and excludes direct contact of metal and the corrosive environment. The thickness of this film is usually 5-6 nm. Owing to the oxide film, titanium and it’s alloys are not corroded in the atmosphere, in fresh and sea water, they are stable in organic acids, and are widely used in various fields of science and technology. Unfortunately, the manufacture of titanium products and it’s alloys has a technological features. The high chemical activity of molten titanium leads to the alpha case formation in the casting of products. There is a sharp decrease of the technological plasticity of titanium and titanium’s alloys by reason of alpha case formation. It is necessary to investigate the chemical processes occurring during the manufacture of magnesium oxide-based mold and casting titanium products to prevent the formation of alpha case. This problem can be solved with the help of plasma methods for coating forms [1-11].

2. Processes occurring during the manufacture of form based on magnesite oxide and casting titanium products
Stage 1: preparation of the starting mixture. At room temperature fine crystalline magnesium oxide is chemically active, so it reacts slowly with water:

\[ \text{MgO} + \text{H}_2\text{O} \leftrightarrow \text{Mg(OH)}_2 \]

(at 350 °C magnesium hydroxide decomposes into magnesium oxide and water) magnesium oxide absorbs carbon dioxide:
MgO + CO₂ ↔ MgCO₃
(at 550-850 °C magnesite decomposes into magnesium oxide and carbon dioxide). Calcium oxide (quicklime) interacts with water:
CaO + H₂O ↔ Ca(OH)₂
(at 520-580 °C calcium hydroxide decomposes into calcium oxide and water)
Sodium oxide reacts with carbon dioxide:
NaO + CO₂ ↔ NaCO₃
(at 855 °C melting of the sodium salt of carbonic acid is occurred)

**Stage 2:** calcination with carbon dioxide.

Purge of the mixture with carbon dioxide accelerates the process of chemical binding of water with elements of liquid glass.

Carbon dioxide chemically reacts with liquid glass with heat release according to the equation:

\[ \text{Na}_2\text{O} \cdot n\text{SiO}_2 + m\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + n\text{SiO}_2 \cdot m\text{H}_2\text{O} \]

As a result of this reaction, the liquid glass is destroyed with the formation of soda and a gel of silicic acid, which has high adhesive properties, linking the grains of sand to each other. The grains of the charge are "dressed" in a shell of silicic acid gel or, as they say, a gel film is formed on the grains (the less water in the hydrogel, the stronger the hardening mixture, and when the portion of the attached water is lost, the gel strengthens) [12, 13].

**Stage 3:** drying at 110-200 °C.

110-120 °C - removal of hygroscopic moisture:

\[ 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\uparrow + \text{O}_2\uparrow \]

above 200 °C - the removal of moisture crystalline hydrate, formed in particular when the batch is moistened:

\[ \text{X} \cdot 2\text{H}_2\text{O} \rightarrow \text{X} + 2\text{H}_2\uparrow + \text{O}_2\uparrow \]

150-200 °C - gel dehydration and evaporation of water - formation of silica gel:

\[ \text{H}_2\text{SiO}_3 \rightarrow \text{H}_2\text{O}\uparrow + \text{SiO}_2 \]

Silica gel (dried gel, \( T_m = 1610 \) °C) is a substance that acquires a porous structure and absorbs moisture well. Silica gel has a large specific surface area consisting of -SiOH groups located at a distance of 0.5 nm from each other. These groups are active centers and the activity of a specific lot of silica gel depends on the number and activity of such centers. In the active adsorbent i.e. in which adsorbed on it's surface water is removed, many centers will be active. Such activation occurs when the gel is heated to 150-200 °C.
Stage 4: calcination to 1000 °C.
200 - above 400 °C - the surface area of the silica gel irreversibly decreases:

\[ H_2SiO_3 \rightarrow H_2O↑ + SiO_2 \]

At temperature in the range of 200-400 °C the activity is lost as a result of the formation of Si-O bonds which occurs with the elimination of water. However this stage is reversible. When heated above 400 °C the surface area of the silica gel irreversibly decreases.

800-900 °C - solid phase formation of sodium silicate:

\[ 2Na^+ + SiO_4^{2-} \rightarrow Na_2SiO_4 \]

At temperature above 567 °C iron oxide reacts with sodium carbonate to form sodium monoferrite and carbon dioxide:

\[ Fe_2O_3 + Na_2CO_3 \rightarrow 2NaFeO_2 + CO_2 \]

up to 1000 °C - formation of magnesium metasilicate - enstatite:

\[ MgO + SiO_2 \rightarrow MgO•SiO_2 \]

up to 1000 °C - formation of calcium metasilicate:

\[ CaO + SiO_2 \rightarrow CaO•SiO_2 \]

The reaction products: periclase constitute the main mass of material, also the material contains calcined gel, enstatite, sodium silicate, sodium monoferrite and calcium metasilicate. A porous structure forms.

Stage 5: cooling to 300 ± 25 °C.

With slow cooling molten sodium silicates and other components are sintered with the moldable mixture. The reactions are summarized in Table 1. Here X is a chemical compound containing bound water.

Stage 6: pouring of molten titanium into the form at 1843 °C

Formation of titanates (magnesium, sodium, calcium). For example the formation of magnesium metatitanate at 850 °C:

\[ MgO + TiO_2 \rightarrow MgTiO_3 \]

The properties of certain titanates that can form during the interaction of Ti melt with magnesite (periclase) casting molds are discussed below.

Ti-Mg

In the MgO-TiO_2 system three compounds are known: Mg_2TiO_4, MgTiO_3 (geykilite), and MgTi_2O_5. The reaction between titanate dioxide and magnesium oxide in their equimolecular mixture (1:1) proceeds with the formation of mainly magnesium metatitanate.
Table 1. Characteristic chemical reactions for the corresponding temperatures during cooling of magnesite forms.

| №  | Reaction temperature range, °C | Name of reaction | Characteristics of the reaction |
|----|-------------------------------|------------------|---------------------------------|
| 1  | 20-25                         | Formation of:   | Na₂O•nSiO₂ + mH₂O + CO₂ → NaCO₃ + nSiO₂•mH₂O; MgO + H₂O ↔ Mg(OH)₂; MgO + CO₂ ↔ MgCO₃; CaO + H₂O ↔ Ca(OH)₂; NaO + CO₂ ↔ NaCO₃ |
|    |                               | - gel of silicic acid as a result of blowing the form with carbon dioxide; - magnesium hydroxide; - magnesium salt carbonic acid; - calcium hydroxide; - sodium salt of carbonic acid |
| 2  | 110—120                       | removal of hygroscopic moisture | 2H₂O → 2H₂↑ + O₂↑ |
| 3  | 200-275                       | removal of moisture crystalline hydrate formed in particular when the charge is moistened | X•2H₂O ↔ X + 2H₂O → 2H₂↑ + O₂↑ |
| 4  | 200 - over 400                | silica gel formation | H₂SiO₃ → H₂O + SiO₂ |
| 5  | over 567                      | synthesis of sodium monoferite | Fe₂O₃ + Na₂CO₃ → 2NaFeO₂ + CO₂ |
| 6  | 851-over 1000                 | melting of the sodium salt of carbonic acid | Na₂CO₃ → Na₂O + CO₂ |
| 7  | 800—900                      | solid phase formation of sodium silicate | 2Na⁺ + SiO₄²⁻ → Na₂SiO₄ |
| 8  | 550-850                      | periclase formation | MgCO₃ → MgO + CO₂ |
| 9  | before 1000                   | formation of metasilicates of magnesium and calcium | MgO + SiO₂ → MgO•SiO₂; CaO + SiO₂ → CaO•SiO₂ |
| 10 | 1843 and above                | titanate formation | MgO + TiO₂ → MgTiO₃ |
| 11 | 1843 and above                | formation of titanium oxides | Ti + 2H₂O → TiO₂ + 4H |

**Ti-Ca**

When TiO₂ interacts with CaCO₃ after dissociation of the carbonate, calcium metatitanate is directly formed, and only at temperatures above 1300-1350 °C with an excess of calcium oxide a three-calcium ditiitanate is formed. At temperatures above 1480 °C we can also observe the formation of a titanate of the composition 3CaOTiO₂. Ershov showed that at temperature up to 1300 °C CaTiO₂ (perovskite) is the least basic compound in the CaO-TiO₂ system [14]. At a temperature of 900 - 1200 °C CaTiO₃ is formed from the anatase with higher rate than from rutile. With a content of several percent of iron oxide in the rutile (in the form of a solid solution) the rate of formation of CaTiO₃ from rutile is higher than from pure anatase [15].

**Ti-Al**

Aluminum titanate Al₂TiO₄ as a refractory material with negative thermal expansion up to 600° C and high volume resistance is of practical interest. Aluminum titanate was obtained by double firing a mixture of fine powders (6 microns grain) of aluminum oxide and titanium dioxide initially at 1820 °C, then at 1650 °C. The melting point of Al₂TiO₃ is 1860 °C. It is stable at temperature above 1300 °C; at a temperature of 750 - 1300 °C it decomposes into corundum and rutile.

**Ti-K**

Potassium metatitanate - K₂Ti₃ (molecular weight is 174.10) is formed in the systems K₂O-TiO₂, K₂O-TiO₂-H₂O and K₂O-TiO₂-CO₂. Practically potassium metatitanate is obtained by fusing titanium dioxide or metatitanic acid with hydroxide or potassium carbonate. In the latter case the reaction for
the accumulation of carbon dioxide is reversible like the reaction with the sodium salt but occurs with a lower yield of titanate. The equilibrium is established at 900 °C, the pressure of carbon dioxide is 1 atm. at the ratios:

\[ 0.65\text{TiO}_2 + 0.65\text{K}_2\text{CO}_3 = 0.35\text{K}_2\text{TiO}_3 + \text{ArCO}_2 \]

The formation of potassium metatitanate also occurs when the elemental titanium is fused with potassium hydroxide and nitrate (or chlorate):

\[ 3\text{Ti} + 2\text{KOH} + 4\text{KNO}_3 = 3\text{K}_2\text{TiO}_3 + 4\text{NO} + \text{H}_2\text{O} \]

The heat of formation of \( \text{K}_2\text{TiO}_3 \) is 384.6 kcal / mol.

Anhydrous potassium metatitanate is a yellowish white crystalline mass. It crystallizes in the tetragonal system \((a = 547, c = 1660 \text{ pm})\). Density is 3.58 g/cm\(^3\) at 20 °C. Melting point is 8160 °C. The dielectric constant is 16.5; refractive index is 1.910.

Potassium ditantate \( \text{K}_2\text{Ti}_2\text{O}_5 \) (molecular weight 254.00) is formed by heating a mixture of titanium dioxide and potassium carbonate at molar ratio of 2:1. Dititantate potassium is a brilliant needle-shaped crystals. Density is 3.485 g/cm\(^3\) at 15 °C. Melting point is 9800 °C. The refractive index is more than 1.74. Crystals of potassium dititanate are weathered in the air. In water dititanate does not dissolve; decomposes with acids.

Potassium hexachitanate \( \text{K}_2\text{Ti}_6\text{O}_3 \) is colorless fibrous crystals with a melting point 13700 °C.

For the analysis of chemical reactions that can lead to the formation of an alpha case layer a calculation of the temperature at the "metal-form" boundary is carried out using the Fourier thermal conductivity equation \([16-21]\). In Fig. 1 there is showed the temperature distribution at the "metal-form" interface and the temperature intervals in which the chemical reactions listed in Table 1 are indicated.

\[ T, \circ\text{C} \]

\[ t \times 10^{-3}, \text{s} \]

**Figure 1.** Temperature distribution at the "metal-form" interface and the temperature intervals in which the chemical reactions listed in Table 1 are indicated.
3. Conclusions
Comparison of the obtained data allows us to consider the following model for the alpha case formation. The source of oxygen supply to the surface of the casting can be compounds of active metals. When molten titanium is poured into the mold due to low thermal conductivity the mold is heated unevenly. At temperature above 840 K, reactions 5-9 from Table 1 begin. The resulting carbon dioxide and active metal compounds migrate to the more heated regions adjacent to the surface of the casting. The increased concentration on the surface of the O, Si, Ca, Na forms promotes the reactions to form active metal titanates. In some cases due to the reversibility of the reactions this leads to the formation of rutile. At high temperature the bound water forms carbon dioxide which in turn comes into various reactions with the active metals and titanium. When temperatures favorable for the formation of rutile from various compounds on the surface of the casting are reached, phase transformations of oxygen solutions in titanium occur.

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