

Communications

Solubility of TiN in Continuous Casting Powders

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Synthetic fluxes are routinely used during the continuous casting of steel from the tundish to the mold. It is well known that the performance of the fluxes can greatly affect caster operations in terms of both operation and product quality. The major functions of tundish fluxes are the thermal insulation of steel, protection of the steel from the atmosphere, and the absorption of inclusions. These slags may also help to partially remove some inclusions from the steel.

For the casting of steels containing titanium, the main inclusions of interest are titanium nitride, carbide, and carbonitride. These titanium-based inclusions affect the surface quality of the steel. They also have a deleterious effect on the mechanical properties and weldability. Therefore, it is important to control or, possibly, to remove these inclusions from the steel. For removal of titanium nitride inclusions, a flux which wets and absorbs a significant amount of these inclusions must be used. When a titanium nitride inclusion contacts with the tundish slag, it may dissolve in the slag if the solubility of the inclusion in the slag is very high and there is no kinetic restriction. Therefore, in order to select an appropriate flux composition for inclusion removal, it is necessary to have the information on the interactions between the inclusions and the fluxes. The solubilities of titanium nitride-based inclusions in some common ladle and tundish and mold fluxes have not been previously investigated. Because of its importance to the inclusion removal during continuous casting, the solubilities of titanium nitride in the tundish and mold fluxes were measured and are reported in this communication.

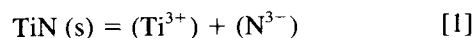
Several laboratory investigations have been carried out on the thermodynamics and kinetics of the dissolution of nitrogen in CaO-Al₂O₃,^[1-4] CaO-Al₂O₃-SiO₂,^[5,6] CaO-SiO₂,^[7] CaO-SiO₂-CaF₂,^[8] SiO₂-Na₂O,^[9] CaO-B₂O₃,^[10] and CaO-Al₂O₃-TiO₂.^[11] Most of these experiments were done by equilibrating a slag or a slag-metal system with a gas phase containing nitrogen under a controlled oxygen pressure. The results of these investigations show that the solubility of nitrogen in these slags in equilibrium with nitrogen gas is small and increase with decreasing oxygen pressure. The solubility also decreases with increasing basicity.

There are no data available on the solubility of titanium nitride in the slags. However, the phase relations in the system Si₃N₄-SiO₂-MgO were studied by Lange^[12] at 2023 K, and only the present phases were identified by X-ray studies. A similar study was done by Land *et al.*^[13] at 2073 K on the Si-Al-O-N system.

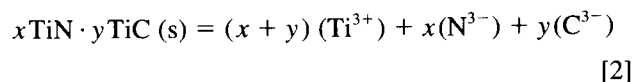
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For example, when a titanium nitride inclusion comes in contact with molten slag, titanium nitride may dissolve in the slag according to the overall reaction



Similarly, the reaction for the dissolution of titanium carbonitride may be written as



where x and y are the mole fractions of TiN and TiC in titanium carbonitride, respectively. For Reactions [1] and [2], it is assumed that nitrogen, titanium, and carbon dissolve in the slag as a free nitride, titanium, and carbon ions, respectively. Similar reactions can also be written if nitrogen, titanium, and carbon ions are incorporated into a network in the slag. The extent of the reaction will depend on the nitride and titania capacity of the slag if there is no kinetic restriction. In the case of titanium carbonitride, the extent of the dissolution reaction will depend on the titania, nitride, and carbide capacity of the slag.

A slag-nitride or slag-carbonitride equilibration technique was used to determine the solubility of titanium nitride and carbonitride in different slags. Pellets of titanium nitride were made by compressing very fine powder of titanium nitride (-325 mesh). They were then sintered at 1923 K under a flowing nitrogen atmosphere for 24 hours. Similarly, titanium carbonitride pellets were made by mixing desired ratios of titanium nitride and titanium carbide and sintering at 1923 K for 24 hours. The formation of titanium carbonitride was revealed by X-ray studies on the samples. The formation of titanium carbonitride is given elsewhere.^[14]

The CaO-Al₂O₃, CaO-Al₂O₃-SiO₂, and the mold and tundish slags were prepared from a mixture of the reagent grade CaO, Al₂O₃, SiO₂, *etc.* and then premelted in recrystallized alumina or molybdenum crucibles at 1873 K under a flowing argon atmosphere. The average chemical compositions of the tundish and mold slags are given in Table I.

A schematic of the experimental apparatus is shown in Figure 1. For the nitride-slag equilibration, a recrystallized alumina reaction tube 44 cm in diameter and 116 cm in length with gas tight seals at both ends was used in a carbon resistance furnace. The seals were fitted with a thermocouple inlet, a gas inlet, and a gas outlet. The temperature of the hot zone was controlled within 3 K and measured with a Pt-6 pct Rh/Pt-30 pct Rh thermocouple. The temperature of the hot zone was also

Table I. Compositions of the Mold and Tundish Fluxes Used in the Experiments

	Tundish Flux	Mold Flux
CaO	40.2	37.85
Al ₂ O ₃	29.45	2.35
SiO ₂	8.5	45.11
MgO	14.60	1.82
TiO ₂	7.25	8.66
MnO	—	4.19

measured before the experiments with another thermocouple. For each experiment, 10 grams of slag and 3 grams of nitride were used. The slag and nitride were placed in an alumina or a molybdenum crucible. Then the crucible, with its contents, was suspended in the hot zone of the furnace. During the experiments, 300 cc/min argon was injected into the reaction tube. The argon gas was cleaned in the usual manner by passing through DRIERITE,* copper chips heated to 623 K,

*DRIERITE is a trademark of Drierite Company, Xenia, OH.

and magnesium perchlorate. After the desired reaction time, the sample was quenched and prepared for chemical analysis. A part of the slag was dissolved, and the titanium nitride or carbonitride particles were separated from the solution. The solution was analyzed for total nitrogen by the "kehjldal" method. Atomic adsorption spectrometry was used to analyze the slag for its constituents. A part of the sample was examined under a scanning electron microscope.

Initial experiments were done as a function of time in order to determine the equilibration time. Calcium aluminate slag (41 wt pct CaO, 59 wt pct Al_2O_3) saturated with $CaO \cdot Al_2O_3$ was equilibrated with titanium nitride for 7, 8, and 9 hours at 1873 K. It was found that the slag samples approximately contain 0.0697 wt pct nitrogen, and therefore, all the titanium nitride slag equilibration experiments were done at 8 hours.

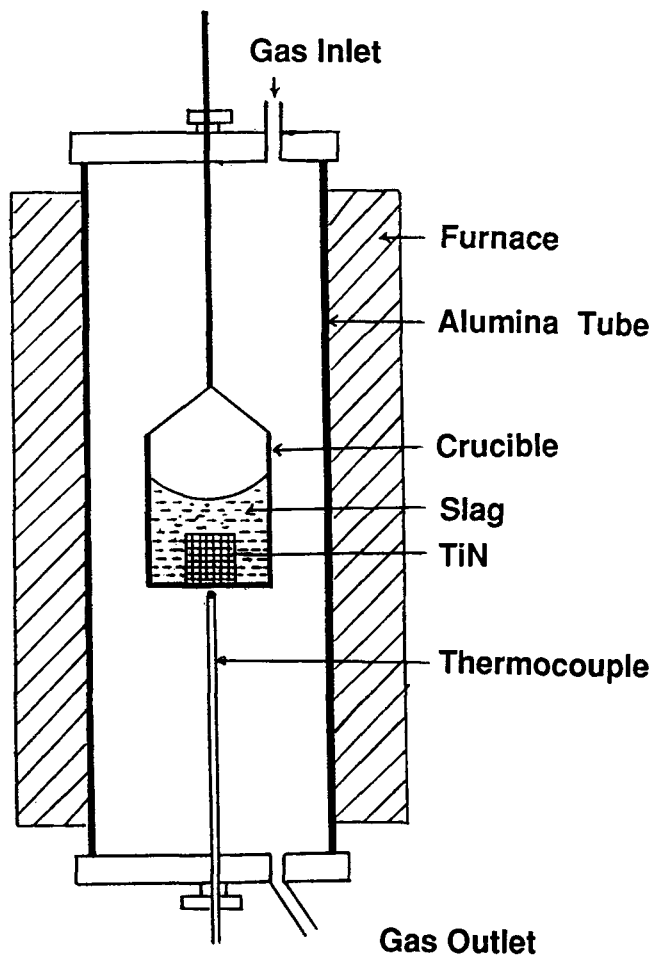


Fig. 1—Schematic of the experimental apparatus.

In a series of experiments, pure solid TiN pellet was equilibrated with $CaO \cdot Al_2O_3$ -saturated $CaO-Al_2O_3$ slag containing 10 wt pct SiO_2 at 1873 K. It was found that the average nitrogen content of the slag was 0.075 wt pct (0.332 wt pct TiN). The slag was free of nitrogen and titanium initially. Therefore, the mole ratio of titanium to nitrogen must be 1, if the dissolution of titanium nitride occurs according to Reaction [1] and there is no nitrogen pickup from the gas phase of purified argon. The sample was also analyzed for titanium. It was found that the titanium content of the slag was slightly lower (0.247 wt pct) than the value calculated from the assumption that all the nitrogen comes from the dissociation of titanium nitride. Similar experiments were done with the calcium aluminate slag containing 20 wt pct SiO_2 . About 0.45 wt pct titanium nitride was dissolved in the slag. The experimental results indicate that the solubility of titanium nitride in calcium aluminate-based slags is low and the solubility increases with increasing the silica content of the slag. The experimental results are summarized in Table II.

The solubility of titanium carbonitride in calcium aluminate slag was also measured. Again, calcium aluminate slag saturated with $CaO \cdot Al_2O_3$ was equilibrated with a titanium carbonitride pellet containing 80 wt pct TiN and 20 wt pct TiC at 1873 K. It is found that the slag contains 0.0357 wt pct nitrogen. This sample was not analyzed for carbon.

After the experiments, the nitride slag interface was examined under a scanning electron microscope. Micrographs, shown in Figure 2, indicate that the titanium nitride pellets were not very dense, and therefore, slag penetrated into the pellets. In some cases, the titanium nitride particles were distributed throughout the slag. They also indicate that the titanium nitride particles were wetted by the calcium aluminate-based slags. However, it was not possible to determine the degree of wetness. The same titanium nitride pellets were used by the authors for the measurements of the solubility in pure iron. During these experiments, the metal was not penetrated into the pellets. Therefore, the contact angle between the titanium nitride and calcium aluminate slags is much lower than the one between the titanium nitride and steel. Only a titanium titanium peak was found in the X-ray energy

Table II. Experimental Results on the Solubility of Titanium Nitride, Titanium Carbonitride, or Silicon Nitride in Slags at 1873 K

Slag Composition	Dissolved Nitride or Carbonitride
41 pct CaO-59 pct Al_2O_3	0.31 pct TiN
36 pct CaO-54 pct Al_2O_3	0.33 pct TiN
41 pct CaO-59 pct Al_2O_3	0.20 pct TiC(N) (80 pct TiN-20 pct TiC)
Tundish flux	0.37 pct TiN
Mold flux	0.45 pct TiN
Mold flux	0.38 pct TiC(N) (80 pct TiN-20 pct TiC)
41 pct CaO-59 pct Al_2O_3	0.23 pct Si_3N_4
30 pct CaO-40 pct Al_2O_3 - 30 pct SiO_2	0.78 pct Si_3N_4

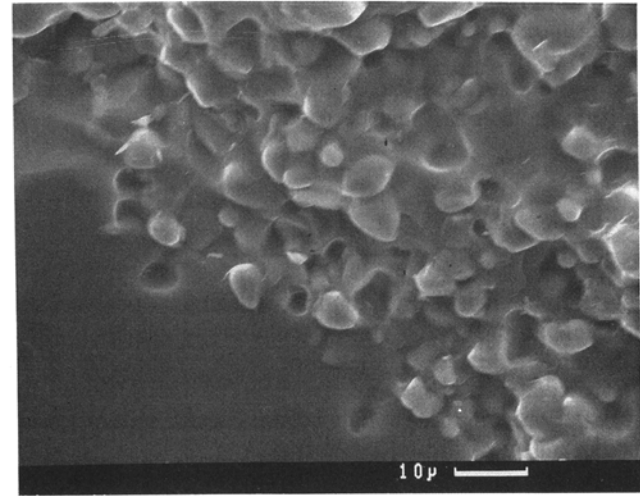
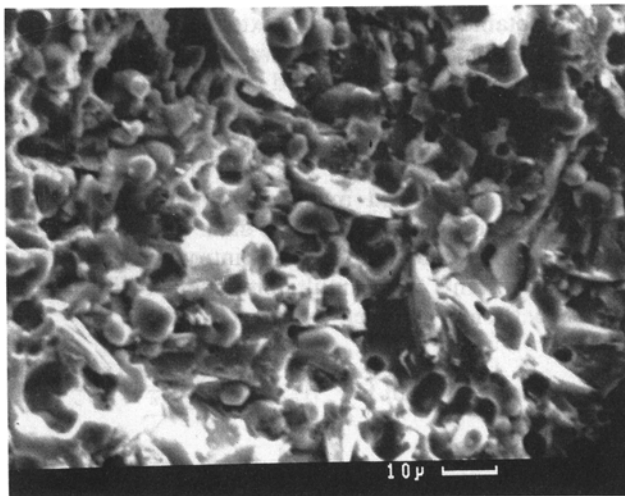
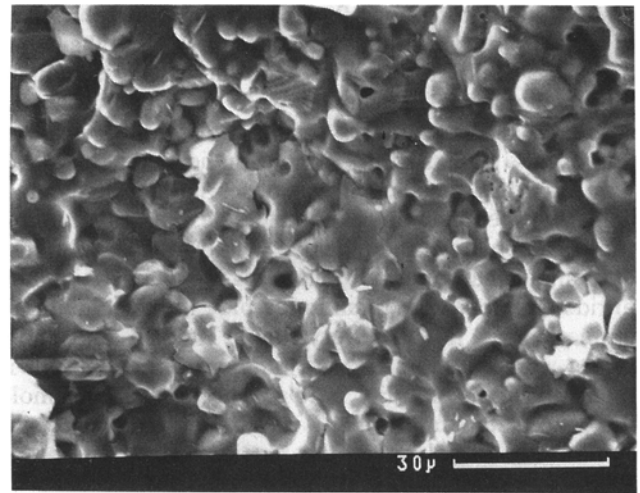
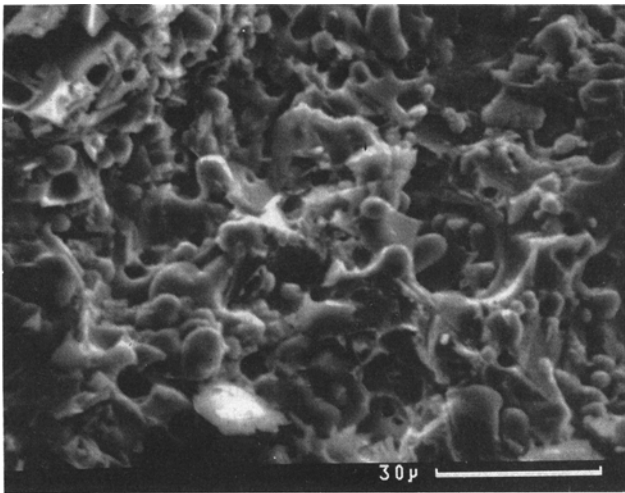


Fig. 2—Micrographs taken from a calcium aluminate slag that equilibrated with a TiN pellet.

Fig. 3—Micrographs taken from the mold flux equilibrated with TiN.

spectrum taken from the particles in the slag, which indicates that they were titanium nitride.

Experiments were carried out with the tundish and mold slags used in industry. The compositions of these slags were received from Allegheny Ludlum Steel Corporation (Brackenridge, PA). These slags react with containers such as alumina, lime, or magnesia crucibles. In order to maintain the constant slag composition, these experiments were carried out in molybdenum crucibles under an argon atmosphere. The tundish flux was equilibrated with titanium nitride pellet at 1873 K for 8 hours. It was found that the slag contained 0.084 wt pct nitrogen. A pure solid titanium nitride pellet was equilibrated with the mold flux at 1873 K. The nitrogen content of the slag was 0.102 wt pct. The mold flux was also equilibrated with TiN-20 wt pct TiC pellet at 1873 K. It was found that the sample contained 0.068 wt pct nitrogen. After the experiments, the samples were examined under the scanning electron microscope. Typical micrographs taken from the mold flux are shown in Figure 3. Again, it was found that the tundish and mold fluxes wet the titanium nitride. The X-ray energy spectrums taken from the bulk tundish and mold fluxes showed only the peaks

corresponding to the major components. However, only a peak corresponding to the titanium was found in the spectrum taken from titanium nitride particles.

Since dense titanium nitride pellets were unavailable, a few experiments were made by equilibrating silicon nitride with $\text{CaO} \cdot \text{Al}_2\text{O}_3$ -saturated $\text{CaO-Al}_2\text{O}_3$ slag. The slag was also analyzed for nitrogen. It was found that the sample contained 0.09 wt pct nitrogen. The solubility of silicon nitride was also measured in a slag containing 30 wt pct CaO, 30 wt pct SiO_2 , and 40 pct Al_2O_3 at 1873 K. It was found that the slag contained 0.31 wt pct nitrogen. After the experiments, the nitride-slag interface was examined under a scanning electron microscope, indicating that the silicon nitride did not react significantly with the slag. The energy-dispersive X-ray spectrum indicates the presence of silicon in the inclusion and calcium and aluminum in the bulk slag. The X-ray spectrums were also taken a few microns away from the silicon nitride-slag interface; however, no silicon peaks were found. The concentration of dissolved silicon due to the dissolution of silicon nitride was very difficult to detect.

The solubility of titanium nitride in calcium aluminate-based slags was measured at 1873 K using a slag-nitride

equilibration technique. It is found that the solubilities of titanium nitride in these slags are low (less than 1 wt pct). The solubility increases with increasing silica content of the slag. The samples were examined under the scanning electron microscope. The scanning electron microscope studies on the samples indicate that the pellet was wetted by the slag. It was observed that the contact angle between calcium aluminate slags and titanium nitride is much lower than the one with iron. The solubility of titanium carbonitride containing 80 wt pct titanium nitride and 20 wt pct titanium carbide in the calcium aluminate slags is also very low. Tundish and mold fluxes were equilibrated with titanium nitride, and it is found that the solubility is low. The tundish and mold fluxes wet titanium nitride. A very small amount of silicon nitride dissolves in the calcium aluminate-based slags.

Under current experimental conditions, the solubilities of titanium nitride in the calcium aluminate-based slags and tundish and mold fluxes used are low (less than 1 pct). Therefore, in order to remove these inclusions from the steel, the fluxes that wet and absorb titanium nitride inclusions must be used.

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An Assessment of the Thermodynamic Properties of Liquid Quaternary Alloys with the Wilson Equation

DONG-PING TAO

Activity coefficients for the liquid phase can be calculated from any one of a number of equations. Although these equations were usually derived by their advocates from theoretical considerations, they must be considered to be largely empirical, since the constants must be obtained from the experimental data of lower order systems to estimate the thermodynamic properties of a higher order system.^[1] However, a significant feature of the Wilson equation is that the equation for a multicomponent solution requires only constants which can be obtained from binary mixture data,^[2] which provides an important economic advantage, since the amount of experimental work required to characterize a multicomponent solution is thereby very much reduced. Therefore, the purpose of this work is to show the advantage of the Wilson equation for liquid multicomponent alloys and make a comparison of it with another one on multicomponent data.

The Wilson equation does not introduce any specific ternary constants in its multicomponent form. The activity coefficient is given by^[3,4]

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^n A_{ji} x_j \right) - \sum_{j=1}^n \frac{A_{ij} x_j}{\sum_{k=1}^n A_{kj} x_k} \quad [1]$$

where γ_i is the activity coefficient of component i , x_j the molar fraction of component j , and A_{ji} or A_{ij} the binary constant. To examine the suitability and reliability of the above equation for liquid multicomponent alloys, the experimental data of activity of component Cd in liquid Cd-Bi-Pb-Sn alloys are employed.^[5] Let components Cd = 1, Bi = 2, Pb = 3, and Sn = 4; thus, the activity coefficient of component 1 in a quaternary system 1-2-3-4 can be written from Eq. [1] as

$$\begin{aligned} \ln \gamma_1 = & 1 - \ln (x_1 + A_{21}x_2 + A_{31}x_3 + A_{41}x_4) \\ & - x_1 / (x_1 + A_{21}x_2 + A_{31}x_3 + A_{41}x_4) \\ & - A_{12}x_2 / (A_{12}x_1 + x_2 + A_{32}x_3 + A_{42}x_4) \\ & - A_{13}x_3 / (A_{13}x_1 + A_{23}x_2 + x_3 + A_{43}x_4) \\ & - A_{14}x_4 / (A_{14}x_1 + A_{24}x_2 + A_{34}x_3 + x_4) \quad [2] \end{aligned}$$

The 12 binary constants in Eq. [2] can be obtained from the activities of the six liquid binary alloys Cd-Bi, Cd-Pb, Cd-Sn, Bi-Pb,^[6] Bi-Sn,^[7] and Pb-Sn.^[8] The calculation steps are as follows.

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