1. Introduction

In the field of steelmaking, tellurium (Te) is mainly used as an alloying element in resulfurized free-machining steel to improve the mechanical properties and the machinability of resulfurized free machining steel. Resulfurized free machining steel is becoming increasingly important as a substitution for leaded free machining steel, whose environmental burden has received serious consideration recently. Resulfurized free machining steel contains dispersed globular MnS inclusions, which contribute to its high machinability by inducing additional stress around these inclusions and promoting crack formation during machining processes.\(^1\) Those inclusions, however, are severely elongated during the hot-rolling process and result in anisotropic mechanical properties of the steel. Tellurium is added in order to overcome this problem. Since tellurium has a chemical affinity toward manganese as does sulfur, it forms MnS–MnTe eutectic inclusions, where MnTe-rich layers surround MnS-rich cores.\(^2\)\(^4\) According to the phase diagram of the MnS–MnTe pseudo-binary system,\(^5\) those inclusions have low liquidus temperature. It is then considered that during the hot rolling process, a tellurium-rich liquid phase forms around the inclusion and deforms sacrificially, which results in a more globular MnS inclusion for the core MnS.\(^2\)\(^6\) Other possible mechanisms in addition to the above-mentioned sacrificial deformation have also been proposed.\(^3\) This globularization is also considered to enhance the ability of MnS inclusion to improve machinability.\(^3\)

Tellurium is also known as a strong surface-active element in molten iron. Ogino et al. performed systematic studies on the effect of four chalcogens (oxygen, sulfur, selenium, and tellurium) on the surface tension of molten iron and its wettability on alumina, revealing that tellurium has the strongest effect among them.\(^7\) Related to these properties of surface tension and wettability, several interesting phenomena caused by tellurium addition into molten iron have been reported, such as acceleration of the removal of alumina inclusions from molten iron,\(^8\) agglomeration and floatation of graphite from molten Fe–Si–C alloy,\(^9\) and retardation of the dissolution of nitrogen into molten iron.\(^10\) These reports show the possibilities of new applications of tellurium. Recently, Kim et al. used tellurium to change the interfacial energy between molten tin and molten salt and investigated its effect on the behaviors of metal emulsification.\(^11\) Applications based on changing the interfacial properties between molten iron and molten slag and controlling the emulsification behavior in actual steelmaking processes should also be possible.

In spite of the aforementioned usefulness of tellurium in the steelmaking industry, the thermodynamic properties

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**Thermodynamic Property of Tellurium in Molten Iron Measured by the Transpiration Method**

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Tellurium is an important alloying element in free-machining steel, but its thermodynamic properties in molten iron are not well understood. In the present study, the standard Gibbs energy (\(\Delta G^\circ\)) for the dissolution of tellurium gas into molten iron was determined in the temperature (T) range from 1 823 to 1 873 K by a vapor-liquid equilibration technique, in which the transpiration method was used to control the vapor pressure of tellurium. This relationship is expressed by the following equations:

\[
\text{Te}(g) = \text{Te}(1 \text{ mass}% \text{ in Fe})
\]

\[
\Delta G^\circ = (-147 000 \pm 6 000) + (53.6 \pm 3.2)T \text{ J/mol}
\]

We quantitatively confirmed that tellurium is thermodynamically less stable than oxygen or sulfur in molten iron. We also found a correlation between the standard Gibbs energy for the dissolution of chalcogens into molten iron and the standard Gibbs energy for the formation of the respective iron-chalcogenides.

**KEY WORDS:** thermodynamics; tellurium; molten iron; vapor-liquid equilibrium; transpiration method.
of tellurium in molten iron or steel are poorly understood. To the best of our knowledge, the only pertinent study is by Ishii et al. They investigated the effect of the four chalcogens on the solubility limit of nitrogen in molten iron and obtained the corresponding interaction parameters. However, they argued that the reliability of the value is relatively low because of the large composition changes during the experiments by the evaporation of tellurium from molten iron. This seems to be one of the reasons why measurement of the thermodynamic properties of tellurium in molten iron is difficult and hence rarely conducted. To obtain reliable results for the thermodynamic properties of tellurium in molten iron, it is necessary to overcome this problem. Another reason may be a difficulty in the experimental treatment of elemental tellurium itself because of its high vapor pressure and toxicity.

Other researches available are rather phenomenological. Wanibe et al. investigated evaporation rates of tellurium from molten iron in various conditions and showed that they are relatively fast among alloying elements used in molten iron. This suggests that tellurium in molten iron is thermodynamically unstable, but no quantitative information has been obtained. Okayama et al. investigated the elution behavior of tellurium from molten iron into slags, revealing the distribution ratio of tellurium to be larger than that of sulfur. The reason for this may also be attributed to the instability of tellurium in molten iron.

This situation, where thermodynamic properties of tellurium in molten iron are hardly known, makes the use of tellurium in the steelmaking industry difficult. As one can estimate from the researches by Wanibe et al. and by Okayama et al., a substantial amount of tellurium may be lost from molten steel through evaporation to the atmosphere or elution into the slag during real steelmaking processes. The fact that tellurium is relatively expensive as an alloying element and its market price is unsettled nowadays may lead to an increase in or instability of production costs. Moreover, since the effects of tellurium addition mentioned above have been reported to be sensitive to its content in molten iron, it is quite important to control it precisely during the various processes. To overcome these problems, an understanding of the thermodynamic properties of tellurium in molten iron is necessary.

Our group has developed an experimental method utilizing the volatility of tellurium. Although some results were already presented previously, we successfully obtained an understanding of its fundamental thermodynamic property, the standard Gibbs energy for the dissolution of tellurium into molten iron. In this paper, we report the methodology and the results in detail, and carefully discuss their validity. In addition, we compare our results with previously-reported ones on oxygen and sulfur, and show an interesting relation between thermodynamic properties of chalcogens in molten iron and those of the respective chalcogenides.

2. Experimental

2.1. Equilibration Experiment

Thermodynamic properties of tellurium in molten iron were investigated by a vapor-liquid equilibrium technique, using the transpiration method to control the vapor pressure of tellurium in the atmosphere. Miki et al. applied a similar method for measurement of the thermodynamic property of phosphorus in molten silicon. Figure 1 shows a schematic of the experimental apparatus. It has two heating zones: in the upper zone, about 4 grams of granular tellurium (99.99%, 30 μm pass) was heated to a constant temperature in a cylindrical graphite container (20 mm OD, 11 mm ID and 50 mm H). Atmospheric gas (Ar + 3% H2) was passed over it at a constant flow rate so that tellurium vapor was generated with a constant vapor pressure. This is the transpiration method. Carbon dioxide and water in the atmospheric gas were removed by calcium carbonate and magnesium peroxide, respectively, before it was supplied into the system. In the lower zone, 2.0 grams of electrolytic iron (99.9%) was contained in an alumina crucible (99.7%, 15 mm OD, 12 mm ID and 30 mm H). The thickness of the molten iron in the crucible is about 10 mm. The sample was heated to the molten state, kept at a constant temperature, and equilibrated with tellurium gas coming from above. The existence of an intermediate compound between Al2O3 and TeO2 has been reported, but it hardly seems to form in this experiment since the activity of TeO2 should be extremely low due to the strongly reducing condition by the mixture gas of argon and hydrogen. Figure 2 is an enlarged view of the container of tellurium. Graphite was chosen as the material because it does not react with tellurium. The gas pipe made of stainless steel and the graphite container were joined with a threaded coupling joint so that they could be disassembled after each heating and the loss in mass of

![Fig. 1. The experimental apparatus. (Online version in color.)](image)
granular tellurium could be measured. A gasket made from a sheet of expanded graphite was placed between the coupling joint and the graphite container in order to seal the system properly. The graphite container, the gas pipe of alumina, and a block of porous alumina were glued together with an alumina adhesive.

The experiments were performed in the following procedures: (1) the apparatus was prepared as illustrated in Fig. 1; (2) atmospheric gas started to flow at a constant rate; (3) the temperatures of the granular tellurium and the lower hot-zone were increased to each target temperature over the course of 3 h, simultaneously; (4) the system was equilibrated for 16–32 h. Since diffusion coefficients \((D)\) of solutes in molten iron are generally on the order of \(10^{-5}\) cm/sec, diffusion distances \((\sim \sqrt{Dt})\) would be about 1 cm for \(t = 16\) h, that is, approximately equal to the thickness of the sample in this experiment. Therefore, this range of experimental duration should be long enough for the system to reach at equilibrium even if any other kind of mass transfer but diffusion does not take place at all in the molten iron; (5) After equilibration, the gas lance was pulled up to the highest position in the reaction tube in order to solidify molten iron without leaking tellurium gas outside. In that position, the temperature of the atmosphere around the sample should be several hundred kelvins, which should enable the sample to solidify quickly enough to prevent tellurium in the sample from escaping by evaporation. The granular tellurium was also cooled in this procedure simultaneously; (6) Finally, when the temperature of the granular tellurium decreased to about 400 K, the gas lance was taken out from the reaction tube. Subsequently, the solidified iron was taken out from the crucible and quenched in water.

Figure 3 shows the partial pressure of various species of tellurium gas in equilibrium with pure solid tellurium in a temperature range just below the melting point of tellurium as calculated with FactSage thermochemical software.\(^{20–22}\) Te\(_2\)(g) is shown to be the dominant specie generated in the upper zone. If we make an approximation that Te\(_2\)(g) is the only specie and assume the partial pressure of tellurium is constant during an experiment, the partial pressure of tellurium obtained by the transpiration method can be obtained by dividing the total number of moles of generated tellurium gas by that of carrier gas (or atmospheric gas in the following equilibration experiments) transferred. Then it can be written as the following equation:

\[
P_{\text{Te}} = \frac{\Delta mRT_{\text{R}}}{2A_{\text{Te}}Ft} \tag{1}
\]

where \(\Delta m\) is the loss in the mass of granular tellurium during an experiment, \(R\) is the gas constant, \(T_{\text{R}}\) is an ambient temperature where the flow rate of gas is measured (room temperature), \(A_{\text{Te}}\) is the atomic mass of tellurium, \(F\) is the flow rate of the carrier gas, and \(t\) is experiment duration. Here we used the equation of state of an ideal gas and assumed that the partial pressure of tellurium was much smaller than that of the carrier gas (= 1 atm).

Figure 4 shows the simulated decomposition behavior of various species of tellurium gas generated at 673 K by
equilibrium evaporation from pure solid tellurium with the increase in temperature under 1 atm calculated using FactSage thermochemical software. According to this, in our experiments, Te(g) and the other polyatomic species decompose as they descend towards the lower hot zone, and almost completely turn into Te(g), eventually. Therefore, the partial pressure of tellurium in the lower hot zone can be written as the following equation:

\[ P_{Te} = \frac{\Delta mRT_e}{A_{Te}F_t} \]  

That is, \( P_{Te} \) is just as twice as \( P_{Te} \), given by Eq. (1). It should be noted that a vapor pressure obtained by either of those equation is an apparent one; generally, it has a negative dependence on the flow rate of the carrier gas, and is different from the true one. If the flow rate is too low, an apparent one becomes higher than the true one. If it is too high, on the other hand, an apparent one becomes lower than the true one. If the flow rate is in the intermediate range, the dependence on the flow rate almost disappears, and an apparent vapor pressure may coincident with the true one. Since this dependence is generally unique for each experimental system, we also investigated this dependence of our system in preliminary experiments, in order to find the proper flow rate for the equilibrium experiments. For these experiments, we used argon gas without hydrogen as a carrier gas.

We also found it very important to properly control the temperature profile of the system, particularly between the two heating zones, in order to prevent the deposition of tellurium gas there. There must be a monotonic temperature increase from the upper zone to the lower zone.

2.2. Chemical Composition Analyses

After the experiments, the samples were subjected to a chemical composition analysis after removing the oxidized films, which seemed to form during the cooling step in the outside of the furnace, and possible contamination on the surface by minutes of acid cleaning. In addition to tellurium content, aluminum and oxygen content in some of the samples were analyzed in order to make it sure that contamination either from the atmosphere or from the crucibles is not significant. The amounts of tellurium and aluminum in the samples were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS7700, SII NanoTechnology, Japan). Particularly for tellurium, the palladium coprecipitation method\(^\text{(23)}\) was adopted to isolate tellurium from an iron matrix, which causes significant interference on the peaks of tellurium in ICP-AES. This method also enabled us to concentrate tellurium and to increase the accuracy of the analysis. Oxygen content was determined by infrared absorption method after combustion (TC600, LECO, U.S.).

3. Result and Discussion

3.1. Vapor Pressure Control by the Transpiration Method

Table 1 shows the conditions and the results of the experiments for investigating the dependence of the apparent partial pressure of tellurium generated by the transpiration method on the flow rate of the carrier gas. \( P_{Te} \), in the table is calculated by Eq. (1). The losses in the mass of granular tellurium during experiments (\( \Delta m \)) are small for its total mass, and thus no significant change in the size or the morphology of granular tellurium was observed. Therefore, we assume that the vaporization rate and hence the partial pressure of tellurium were kept at constant during each experiment. Figure 5 shows the observed dependence of the apparent partial pressure of tellurium gas on the flow rate. As the figure shows, the apparent vapor pressure decreases as the flow rate increases, and becomes almost constant eventually. We have an “intermediate range” described in the previous section where the difference between an apparent partial pressure and the true one becomes minimal in the range of 175–200 ml/min. For the following equilibration experiments, we used 200 ml/min for the flow rate of the atmospheric gas.

| \( T_e (K) \) | \( F \) (ml/min) | Time (h) | \( T_s (K) \) | \( \Delta m \) (mg) | \( P_{Te} \) (\( \times 10^{-5} \text{ atm} \)) |
|---|---|---|---|---|---|
| 663 | 39 | 20 | 312 | 44.5 | 9.33 |
| 666 | 117 | 18 | 305 | 77.4 | 2.58 |
| 666 | 175 | 24 | 304 | 119.5 | 2.27 |
| 663 | 206 | 16 | 312 | 44.3 | 2.27 |

Table 1. Conditions and results of the experiments for investigating the dependence of the apparent partial pressure of tellurium generated by the transpiration method on the flow rate of atmospheric gas.

3.2. Equilibration Experiments between Molten Iron and Tellurium Gas

Table 2 shows the conditions and the results of the equilibration experiments between molten iron and tellurium gas. The errors in tellurium and aluminum content in the table corresponds to the standard deviations of the concentrations of tellurium in the sample solutions measured with ICP-AES. The error in oxygen content is the standard deviation in the results of two different parts of the samples. Aluminum and oxygen contents in the selected samples are not significantly high. Thermodynamic calculation using
available data suggests that there is no chance of formation of Al₂Te₃ or TeO₂ as primary inclusions in these range of oxygen and aluminum contents. Since it seems difficult to decrease them significantly within the framework of our experimental methodology, we reasonably regarded the system as Fe–Te binary and neglected the effect of aluminum and oxygen in this study. Further studies investigating the interaction parameters of these elements on tellurium are necessary to rigorously justify this assumption.

Figure 6 shows the obtained relationship between partial pressure of tellurium in the atmosphere and tellurium content in molten iron at different temperatures. A linear relationship is observed at each temperature within the range of the errors from chemical analysis. This confirms that tellurium gas dissolves into molten iron as a monoatomic gas is expected to from the calculation and that the dilute solution of tellurium in molten iron obeys Henry’s law at least in the range of tellurium content of the present study. There is no significant difference between the results for the experimental durations of 16 and 32 hours at 1 848 K, suggesting 16 hours was enough for the equilibration. Therefore, we combined the data sets and then fit with a single regression line. Since the behavior of mass transport in the system would not change significantly by the temperature variation from 1 823 to 1 873 K, we assume that an equilibrium was achieved also in each experiment at 1 823 and 1 873 K in 16 hours.

### 3.3. Representations of Thermodynamic Property of Tellurium in Molten Iron

The thermodynamic stability of tellurium in molten iron can be expressed as the standard Gibbs energy for the dissolution of tellurium gas into molten iron:

$$\Delta G^0 = -RT \ln \left( \frac{f_{Te} \text{[mass\% Te]}}{P_{Te}} \right) \tag{4}$$

where $f_{Te}$ is the activity coefficient of tellurium in molten iron with 1 mass% standard. As tellurium obeys Henry’s law ($f_{Te} = 1$) as discussed above, the standard Gibbs energy at each temperature can be determined according to Eq. (4) and the slope of the corresponding regression line in Fig. 6. The temperature dependence of the standard Gibbs energy is shown in Fig. 7. The error bars in the figure correspond to standard errors of slopes of the regression lines in Fig. 6. The dependence can be regarded as linear in this range. Thus, the standard Gibbs energy for the reaction expressed in Eq. (3) was determined as the following equation by a linear regression of these three points:

$$\Delta G^0 = (-147 000 \pm 6 000) + (53.6 \pm 3.2)T \ J / \text{mol} \ldots \tag{5}$$

The errors in the above equation correspond to the standard errors of the slope and the intercept of the regression line. It should therefore be noted that they do not include information about the error of the value of $\Delta G^0$ at each temperature.

Another possible route for determining an equation representing the temperature dependence of the standard Gibbs energy would be a linear regression of the values of $\Delta G^0$ calculated using Eq. (4) from the values of $T$, $P_{Te}$, and [mass% Te] at each coordination point in Fig. 6. Taking this route, however, one can’t take into account the difference in reliability of values of slopes obtained from coordination

| $\text{Te}_f$ (K) | $\text{Te}_i$ (K) | Time (h) | $P_{Te}$ ($\times 10^{-5}$ atm) | Te content (ppmw) | Al content (ppmw) | O content (ppmw) |
|------------------|------------------|---------|-----------------|----------------|----------------|----------------|
| 1 823            | 663              | 16      | 4.43            | 12.5 ± 0.6     |                |                |
| 1 823            | 673              | 16      | 7.60            | 19.1 ± 0.5     |                |                |
| 1 823            | 683              | 16      | 11.69           | 31.6 ± 0.8     | 12 ± 5         |                |
| 1 848            | 663              | 16      | 4.36            | 3.05 ± 0.3     |                |                |
| 1 848            | 673              | 16      | 6.98            | 16.7 ± 0.2     |                |                |
| 1 848            | 673              | 16      | 7.12            | 16.7 ± 0.7     | 22 ± 4         |                |
| 1 848            | 673              | 32      | 6.69            | 15.5 ± 0.7     |                |                |
| 1 848            | 683              | 16      | 11.09           | 25.0 ± 0.8     |                |                |
| 1 873            | 663              | 16      | 4.51            | 9.3 ± 0.2      |                |                |
| 1 873            | 673              | 16      | 8.28            | 15.6 ± 0.3     |                |                |
| 1 873            | 683              | 16      | 12.70           | 27.0 ± 0.6     | 18 ± 3         |                |

**Fig. 6.** Relationship between partial pressure of tellurium in the atmosphere and tellurium content in molten iron at different temperature.

**Fig. 7.** Temperature dependence of the standard Gibbs energy for the dissolution of tellurium gas into molten iron. The error bars correspond to standard errors of slopes of the regression lines in Fig. 6.
points with different distances from the center of gravity (the origin, in this case). Therefore, we consider the route described in the previous paragraph to be more appropriate. A representation based on 1 mol% standard is also useful and expressed by the following:

\[
\text{Te(g)} = \text{Te(1 mol\% in Fe)} \quad \Delta G^o = \left( -147,000 \pm 6,000 \right) + \left( 45.2 \pm 3.2 \right) T \text{ J/mol} \quad (6)
\]

3.4. Comparison with Oxygen and Sulfur

As described in the first section, tellurium belongs to the same group of elements as oxygen, sulfur, and selenium. As in Ogino et al., the properties of these four elements are often investigated simultaneously and compared with each other so that one can get more interesting information or a better understanding of their physical origins. Similarly, in this section, the thermodynamic property of tellurium will be compared with those of oxygen and sulfur from some different points of view. To the best of our knowledge, any corresponding information about selenium has not been reported yet.

In order to compare the properties of different elements, it is better to use the 1 mol% standard state for the elements in molten iron instead of the 1 mass% state. Chang et al. summarized a number of standard Gibbs energies for the dissolution of oxygen, nitrogen, and sulfur into various liquid metals. For the dissolution of oxygen into molten iron, the reaction and the standard Gibbs energy are given as follows, respectively:

\[
\text{O(g)} = \text{O(1 mol\% in Fe)} \quad \Delta G^o = -371,000 + 52.2 T \text{ J/mol} \quad (8)
\]

\[
\text{S(g)} = \text{S(1 mol\% in Fe)} \quad \Delta G^o = -353,000 + 80.1 T \text{ J/mol} \quad (10)
\]

Note that we converted the standard states of gas species in the left hand sides from diatomic to monoatomic using the tabulated thermodynamic data. Equations (7), (9) and (11) are plotted versus temperature in Fig. 8. It clearly shows that the thermodynamic stability of tellurium in molten iron is lower than that of oxygen or sulfur over the entire temperature range for steelmaking processes. This is consistent with the above-referenced phenomenological studies in which it is indicated that tellurium is less stable than oxygen or sulfur in molten iron.

3.5. Relation to the Standard Gibbs Energy for the Formation of Compounds

Fitzner found a correlation between the enthalpy of solution of oxygen into liquid transition metals and the standard enthalpy of formation of the respective oxides. In a similar fashion, we may understand the difference among the standard Gibbs energy of dissolution of oxygen, sulfur and tellurium. The standard Gibbs energy of formation of the respective compounds at 1 873 K have been assessed as follows:

\[
\text{Fe(l) + O(g)} = \text{FeO(s)} \quad \Delta G^o = -529,100 + 136.3 T \text{ J/mol} \quad (12)
\]

\[
\text{Fe(l) + S(g)} = \text{FeS(s)} \quad \Delta G^o = -377,000 + 118.6 T \text{ J/mol} \quad (14)
\]

\[
\frac{10}{9} \text{Fe(l) + Te(g)} = \frac{10}{9} \text{FeTe}_{0.9}(s) \quad \Delta G^o = -254,700 + 133.0 T \text{ J/mol} \quad (16)
\]

Here, their enthalpy and entropy terms are shown explicitly. In Fig. 9, the values of Eqs. (13), (15) and (17) at 1 873 K are compared with those of standard Gibbs energy for dissolution of gas species into molten iron, which are expressed as Eqs. (7), (9) and (11), at 1 873 K. Interestingly, the data in Fig. 9 exhibits a clear relation, indicating the existence of a common mechanism among the interatomic interactions in molten iron-chalcogen alloys and those in iron-chalcogenides. A detailed quantitative understanding of any such relationship, however, is beyond the scope of this manuscript.
also suggests that the result of the present study is consistent with the existing data on oxygen and sulfur.

### 4. Conclusion

The standard Gibbs energy for dissolution of tellurium gas into molten iron (1 823 ≤ $T$ ≤ 1 873 K) was successfully determined as follows by means of a vapor-liquid equilibration technique using the transpiration method to control the vapor pressure of tellurium in the atmosphere:

$$\Delta G^\circ = (-147 \ 000 \pm 6 \ 000) + (53.6 \pm 3.2) T \ J / \ mol$$

Comparing this value to the respective values about oxygen and sulfur, we quantitatively confirmed that tellurium is less stable than oxygen or sulfur in molten iron. We also found a clear relation between the standard Gibbs energy for the dissolution of chalcogens into molten iron and the standard Gibbs energy for the formation of the respective iron-chalcogenides.

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