can be explained by two competing mechanisms: the strain hardening effect increasing the yield strength and the Bauschinger effect causing a yield strength drop.

Discussing the Bauschinger effect first, it is much larger in the A steel than in the B steel, and thus, the yield strength drop in the A steel is twice that of the B steel (43 MPa vs 22 MPa) under the strain of piping (Figure 5). This yield strength drop can be explained by the pinning of mobile dislocations due to the presence of fine Nb(C,N) carbonitrides, as suggested by Seeger et al.\[11\]. In the A steel, Ti(C,N) carbonitrides due to the Ti addition here additionally promote the dislocation pinning, thereby leading to the larger Bauschinger effect. On the other hand, the strain hardening effect is much larger in the B steel than in the A steel, as shown in the stress-strain curves of Figure 4. This is because considerable strain hardening occurs in the B steel under the 1.4 pct strain applied during piping, whereas almost no strain hardening results from the 1.6 pct strain in the A steel. This difference in strain hardening of the two steels is attributed to the presence or absence of a yield-point phenomenon. The B steel undergoes considerable strain hardening under strains as small as 1.4 pct because of its continuous yielding behavior, whereas the A steel hardly has any strain hardening because of the yield-point phenomenon. This yield-point phenomenon is also associated with alloy compositions and microstructures. According to Coldren et al.\[12,13\] and Irani and Tither\[14\] by adding molybdenum into HSLA steels, the \(\gamma \rightarrow \alpha\) transformation temperature can be lowered, pearlite formation can be discouraged, and low-temperature transformation products such as acicular ferrite having high dislocation density can be promoted. Because of this high density of mobile dislocations, the yield-point phenomenon does not occur as the movement of dislocations under an applied stress gradually increases and the elastic limit decreases. In this study, the Mo-containing B steel has formed acicular ferrite having high density of dislocations (Figure 3(c)) and is, accordingly, confirmed to have the lower yield strength and the continuous yielding behavior (Figure 4 and Table III). Consequently, in the A steel, the Bauschinger effect after piping is larger due to the precipitation of fine carbonitrides, but little strain hardening occurs because of the yield-point phenomenon. With the Bauschinger effect overriding the strain hardening effect, the yield strength is significantly reduced. On the other hand, since the B steel shows the continuous yielding behavior due to the Mo addition, the strain hardening effect becomes larger, enough to offset the Bauschinger effect. Thus, the yield strength after piping increases rather than drops.

These findings present that two competing mechanisms, i.e., the strain hardening effect increasing the yield strength and the Bauschinger effect decreasing it, are operating and explain the yield strength variations occurring in API-X70 steel plates after piping. Particularly, capitalizing on the fact that the absence of the yield-point phenomenon is associated with the larger strain hardening effect, Mo was added to eliminate or to reduce the yield-point phenomenon. This proves useful in preventing the reduction of yield strength and increases it. In evaluating pipe formability, investigations of the tensile properties including the yield-point phenomenon provide valuable data in addition to the evaluation of the Bauschinger effect.

This work has been supported by 1997 Pohang Iron and Steel Co. (POSCO) under Contract No. 1PD9704001. The authors thank Professor Nack J. Kim, POSTECH, Dr. Ki Yong Park, Dr. Kwang Sup Noh, and Mr. Jung Min Choi, POSCO; and Mr. Jae Eul Kim, Mijoo Steel Co., for their helpful discussion on spiral piping and macrostructural analysis.

REFERENCES


Measurement of the Activity of Boron in Liquid Copper using a Four-Phase Equilibrium Technique

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Boron can be used to deoxidize liquid copper. It can be added as a Cu-B master alloy or as tetraboron carbide (B\(_{4}C\)). Presence of boron as a minor element is known to increase the resistance of copper alloys to corrosive wear. Despite potential application in the metallurgy of copper, there is no reliable experimental information on either the activity of boron in liquid copper or of its effect on the behavior of dissolved oxygen.

The phase diagram of Cu-B system is of simple eutectic type characterized by eutectic temperature of 1286 K and eutectic composition \(\lambda_{B} = 0.133\).\[1\] Phase diagram literature has been reviewed by Chakrabarti and Laughlin.\[1\] There is some uncertainty in the reported values for the eutectic temperature and composition.
Yukinobu et al.\(^{[2]}\) have determined the activity of boron in liquid Cu-B alloys at low concentrations by electromotive force measurement. A cell incorporating calcium aluminate melt as the electrolyte was used. The activities exhibit large positive deviation from Raoult's law. Batalin et al.\(^{[3]}\) have determined partial and integral enthalpy of mixing of the liquid Cu-B alloys in the Cu-rich region at 1790 K by high-temperature calorimetry using high purity copper and amorphous boron as starting materials. Their values for partial enthalpy of boron at low concentrations show large scatter. From their results, the partial heat of mixing of boron at infinite dilution in liquid Cu-B alloys can be estimated as 57.57(±20) kJ/mol\(^{-1}\) using the subregular solution model. Witusiewicz,\(^{[4]}\) using an isoperibol high-temperature calorimeter, has investigated the thermodynamic properties of liquid Cu-B alloys. A value of 45(±10) kJ/mol\(^{-1}\) for the partial enthalpy of mixing of boron at infinite dilution in liquid Cu-B alloys relative to solid boron as the standard state was obtained.

The purpose of this article is to report measurements on dilute Cu-B alloys at 1723 K using a new four-phase equilibrium technique. The method can be considered as an extension of the conventional procedure involving metal-slag-gas equilibration, where the gas phase containing carbon monoxide is pre-equilibrated with graphite to define the carbon and oxygen chemical potentials. Under the reducing atmosphere, liquid diboron trioxide (B\(_2\)O\(_3\)) is partially reduced by graphite generating a liquid Cu-B alloy and carbon monoxide at controlled pressure. After quenching to room temperature, the concentration of B in the liquid copper is measured. The equilibrium boron concentration in copper is measured as a function of the partial pressure of carbon monoxide in the gas phase.

High purity materials (Cu > 99.999 mass pct, B\(_2\)O\(_3\) > 99.99 mass pct, CO > 99.99 pct purity, and graphite of spectral grade) are used. B\(_2\)O\(_3\) was dried first in flowing Ar at 423 K and then under vacuum at 473 K for 4 hours before use. Mixtures of Ar + CO of the desired composition are prepared by mixing metered streams of Ar and CO in a chamber filled with glass beads. Mass flow controllers are used to measure the flow rates accurately.

A schematic diagram of the apparatus used for measurement is shown in Figure 1. Liquid copper is held in a graphite crucible covered by a layer of liquid B\(_2\)O\(_3\) melt. Carbon monoxide or a controlled mixture of Ar + CO is passed over the melt. In preliminary experiments, deposition of carbon was observed in the cooler parts of the vertical alumina tube in which the crucible was placed. Since the carbon deposition generates CO\(_2\) in the gas phase and affects the oxygen potential, the gas phase is re-equilibrated with graphite by passing the gas through a chamber containing graphite chips maintained at the temperature of measurement. A rotating stirrer allows mixing of the metal and slag and accelerates the attainment of equilibrium between the gas and condensed phases. Although the equilibrium is attained in 1.5 hours at 1723 K, the system is maintained at the temperature with stirring for 2.5 hours. After passing over the melt, the gas exits the constant temperature zone through a small orifice in the graphite plug placed below the crucible. The deposition of carbon at furnace exit therefore does not alter the partial pressure of carbon monoxide in the high-temperature zone. The temperature of the metal and slag is measured by a Pt/Pt - 13 pct Rh thermocouple, checked against the melting point of gold. An alumina tube protects the thermocouple. The temperature of the vertical resistance furnace is controlled to ±1 K.

The alumina tube enclosing the reaction chamber is closed at both ends by brass caps with provision for gas ports, stirrer, and thermocouple protection tube. The lower part of the alumina tube is water cooled. After 2.5 hours of equilibration, the stirrer is withdrawn, and metal and slag phase are allowed to separate for 0.5 hours. At the end of each experiment, the crucible is lowered into the water-cooled region. The concentration of boron in copper is determined using inductively-coupled plasma–emission spectrometer. The approach to equilibrium at constant partial pressure of CO is verified from both higher and lower concentrations of boron in liquid copper. Analysis of the slag phase indicated that the concentration of copper in the melt was below the detection level.

The equilibrium concentration of boron in copper at 1723 K at different partial pressures of carbon monoxide in the gas phase is shown in Table I. The same value for the

### Table I. Equilibrium Boron Concentration in Liquid Copper at Different Partial Pressure of Carbon Monoxide in the Gas Phase and Derived Activity at 1723 K

<table>
<thead>
<tr>
<th>(p^c) (Pa)</th>
<th>(X_B)</th>
<th>(a_{B(1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.001</td>
<td>0.0222</td>
<td>0.0757</td>
</tr>
<tr>
<td>0.886</td>
<td>0.0262</td>
<td>0.0883</td>
</tr>
<tr>
<td>0.775</td>
<td>0.0333</td>
<td>0.1097</td>
</tr>
<tr>
<td>0.679</td>
<td>0.0416</td>
<td>0.1336</td>
</tr>
<tr>
<td>0.575</td>
<td>0.0568</td>
<td>0.1746</td>
</tr>
<tr>
<td>0.471</td>
<td>0.0779</td>
<td>0.226</td>
</tr>
<tr>
<td>0.429</td>
<td>0.0975</td>
<td>0.2696</td>
</tr>
<tr>
<td>0.387</td>
<td>0.118</td>
<td>0.3108</td>
</tr>
</tbody>
</table>

\(p^c = 1.013 \times 10^5\) Pa (standard pressure).