Metallurgical Model of Diffusible Hydrogen and Non-Metallic Slag Inclusions in Underwater Wet Welding of High-Strength Steel

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Abstract: High susceptibility to cold cracking induced by diffusible hydrogen and hydrogen embrittlement are major obstacles to greater utilization of underwater wet welding for high-strength steels. The aim of the research was to develop gas–slag systems for flux-cored wires that have high metallurgical activity in removal of hydrogen and hydroxyl groups. Thermodynamic modeling and experimental research confirmed that a decrease in the concentration of diffusible hydrogen can be achieved by reducing the partial pressure of hydrogen and water vapor in the vapor–gas bubble and by increasing the hydroxyl capacity of the slag system in metallurgical reactions leading to hydrogen fluoride formation and ionic dissolution of hydroxyl groups in the basic fluorine-containing slag of a TiO$_2$–CaF$_2$–Na$_3$AlF$_6$ system.

Keywords: underwater wet welding; diffusible hydrogen; slag inclusions; flux-cored wire

1. Introduction

Underwater wet welding is a welding technique commonly used for the construction and repair of ocean-going vessels, oil and gas platforms, and offshore wind turbines. The load-bearing structures of such vessels and installations are often made of high-strength steels [1,2], which pose considerable challenges to welders and the welding processes to obtain the welds exhibiting high levels of strength, ductility, and impact toughness [3,4]. A further issue is that underwater wet welding is susceptible to weld defects like hydrogen-assisted cold cracking, porosity, slag inclusions, and delayed hydrogen embrittlement [5–10]. Consequently, underwater wet welding has found only limited use for critical applications, which requires further study of the mechanism of the appearance of defects.

The appearance of defects during underwater welding is associated with the formation of diffusible hydrogen, active oxygen, and slag in the welding zone [11]. In underwater wet welding, the welding occurs in a vapor–gas bubble [12–14] in which the hydrogen content reaches 85–96% [15]. When welding with coated electrodes and flux-cored rutile wire, the vapor–gas bubble comprises 93–98% H$_2$, 1.5–6% CO, and 0.5–2% CO$_2$ [16]. Hydrogen from the vapor–gas bubble can be absorbed into the liquid weld, which is the major cause of porosity in underwater wet welding. The gas composition of pores in the weld consists of 62–82 wt.% H$_2$, 11–24 wt.% CO, and 4–6 wt.% CO$_2$, depending on the composition of the electrode coating and the welding parameters used [17].

Before dissolution of hydrogen atoms in the liquid weld pool, dissociation of H$_2$O and H$_2$ occurs [18]. At the arc temperature, water (H$_2$O) dissociates according to the following reaction:

\[ \text{H}_2\text{O} = \text{H}_2 + 0.5\text{O}_2 - 260 \text{kJ} \] (at 6000 K)
\[ \lg K_q = \lg \frac{P_{\text{H}_2}P_{\text{O}_2}^{0.5}}{P_{\text{H}_2\text{O}}} \]  

(2)

where \( K_q \) is the reaction equilibrium constant, and \( P_{\text{H}_2}, P_{\text{O}_2}, \) and \( P_{\text{H}_2\text{O}} \) are the partial pressure (Pa) of \( \text{H}_2, \text{O}_2, \) and \( \text{H}_2\text{O} \), respectively.

With further heating of the gas mixture, endothermic reactions of dissociation of the \( \text{H}_2 \) molecules and ionization of the \( \text{H} \) atoms occur.

\[ \text{H}_2 = \text{H} + \text{H} - 463.1 \text{ kJ} \]  

(3)

\[ \text{H}_2 = \text{H}^+ + \text{e} - 1746.7 \text{ kJ} \]  

(4)

Dissolution of molecular hydrogen in the weld pool increases with growth in the partial pressure of the components of the gas mixture according to Sieverts’ law.

\[ [\text{H}] = K_s \sqrt{P_{\text{H}_2}} \]  

(5)

where \([\text{H}]\) is the hydrogen content in the weld in wt.%, \( P_{\text{H}_2} \) is the partial pressure of molecular hydrogen in the gas phase, and \( K_s \) is the solubility constant.

With increases in the immersion depth, the pressure in the vapor–gas bubble increases by about 0.1 MPa for every 10 m of immersion depth, and at a depth of 50 m the total pressure reaches 0.6 MPa. The increase in pressure promotes the dissolution of hydrogen in the weld pool and thus porosity increases [19–23].

One mechanism for diffusible hydrogen reduction is a decrease in the hydrogen partial pressure in the vapor–gas bubble atmosphere, for example, by dissociation of carbonates and fluorides, namely \( \text{Na}_2\text{CO}_3, \text{NaF}, \text{CaCO}_3, \text{CaF}_2, \text{MgCO}_3, \) and \( \text{MgF}_2 \), in the flux-cored wire. To reduce porosity, carbonates \( \text{CaCO}_3 \) and \( \text{MgCO}_3 \) can be added into the electrode coatings. The carbonates dissociate in the vapor–gas bubble with the formation of \( \text{CO}_2 \) and \( \text{CO} \), which reduces the hydrogen partial pressure above the weld pool [24].

A second mechanism for hydrogen reduction is via the chemical reaction of hydrogen and fluorine with formation of HF compounds in reactions with fluorides \( \text{NaF}, \text{CaF}_2, \text{MgF}_2, \text{AlF}_3, \) etc. [25,26]. A linear decrease in the content of diffusible hydrogen \([\text{H}]\) in the weld metal occurs with increases in the content of \( \text{CaF}_2 \) from 0 to 86 wt.%. Increasing \( \text{CaF}_2 \) is a more effective approach for reducing hydrogen than adding \( \text{CaCO}_3 \) to the electrode coating. For example, \([\text{H}]\) content in the weld is 54 cm³/100 g when adding 20 wt.% \( \text{CaCO}_3 \) to the electrode coating, and when adding 20 wt.% \( \text{CaF}_2 \) the \([\text{H}]\) content decreases to 39 cm³/100 g [26].

A third mechanism for hydrogen reduction is an increase of the oxidation potential of the weld pool and solubility of water vapor and OH hydroxyl groups in the liquid slag, in particular, by the addition of hematite \( \text{Fe}_2\text{O}_3 \) with a density of 5.3 g/cm³ [9]. Hematite \( \text{Fe}_2\text{O}_3 \) decomposes under high-temperature conditions with the formation of wüstite \( \text{FeO} \) in the molten slag, which increases the basicity index of the slag; in addition, \( \text{FeO} \) oxidizes the weld pool, which inhibits dissolution of diffusible hydrogen in the weld pool. However, an increase in the oxidizing potential of the slag and the atmosphere of the vapor–gas bubble leads to slag nonmetallic inclusions and oxidation of alloying elements [27–30], which reduces the mechanical properties of the welds [9,31].

The slag basicity index BI is calculated as follows [32]:

\[
\text{BI} = \frac{\text{CaO} + \text{MgO} + \text{BaO} + \text{CaF}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} + 0.5(\text{FeO} + \text{MnO})}{\text{SiO}_2 + 0.5(\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)}
\]  

(6)
The hydroxyl capacity of a $\text{C}_{\text{OH}}$ slag system is determined according to the following equation:

$$
\text{C}_{\text{OH}} = \frac{\% \text{H}_2\text{O}}{\sqrt{P_{\text{H}_2\text{O}}/P^0}}
$$

(7)

where $\text{H}_2\text{O}$ is the content of water vapor in the slag in wt.%, $P_{\text{H}_2\text{O}}$ is the partial pressure of water vapor in the gas phase above the molten slag in the equilibrium state, and $P^0$ is the atmospheric pressure [33]. A ratio for the hydroxyl capacity of $\text{C}_{\text{OH}}$ slag has been proposed in [34,35] as follows:

$$
\log \text{C}_{\text{OH}} = 12.04 - 32.63\Lambda + 32.71\Lambda^2 - 6.62\Lambda^3
$$

(8)

An increase in the basicity index of the slag and hydroxyl capacity can be achieved by adding $\text{CaF}_2$ and cryolite $\text{Na}_3\text{AlF}_6$, which decrease the melting point, viscosity, hydrogen permeability, and density of the slag system [36–41]. The increase in slag basicity and the presence of ion $\text{F}^-$ elevate the solubility of water vapor and promote the ionic binding of the hydrogen atom in OH hydroxyl groups, which leads to a decrease in the content of diffusible hydrogen [42]. The subsequent binding of hydroxyl groups $\text{OH}$ is possible in the polymerization of $\text{AlF}_6^{3-}$ and $\text{AlF}_4^{-}$ anions and the formation of clusters with the bonds $-\text{F}--\text{F}$– and $-\text{Al}--\text{Al}$– [43–45].

Simultaneous implementation of all three mechanisms for the decrease of diffusible hydrogen in underwater wet welding is possible by creating a low-density slag system based on $\text{TiO}_2$–$\text{CaF}_2$–$\text{Na}_3\text{AlF}_6$. It is known that water vapor dissolves in acidic and basic slags following the following ionic reactions [46–48]:

$$
\text{-Si-O-Si-} + \text{H}_2\text{O} = 2(\text{-Si-OH-}) \quad \text{(acidic slag)}
$$

(9)

$$
\text{O}^0 + \text{H}_2\text{O} = 2(\text{OH}) \quad \text{(acidic slag)}
$$

(10)

$$
2(\text{-Si-O-Si-}) + \text{Fe}^{2+} + \text{H}_2\text{O} = \text{-Si-O-Si} + 2(\text{OH}^-) + \text{Fe}^{2+} \quad \text{(basic slag)}
$$

(11)

$$
2(\text{-Si-O-Si-}) + \text{Fe}^{2+} + \text{H}_2\text{O} = 2(\text{-Si-OH-}) + \text{O}^2^- + \text{Fe}^{2+} \quad \text{(basic slag)}
$$

(12)

$$
\text{H}_2\text{O} + 2\text{O}^- = (\text{O}^2^-) + 2(\text{OH}) \quad \text{(highly basic slag)}
$$

(13)

$$
\text{H}_2\text{O} + 2\text{O}^- = (\text{O}^0) + 2(\text{OH}^-) \quad \text{(highly basic slag)}
$$

(14)

$$
\text{H}_2\text{O} + \text{O}^2^- = 2(\text{OH}^-) \quad \text{(highly basic slag)}
$$

(15)

The transition of atomic hydrogen into the weld pool and the formation of diffusible hydrogen $[\text{H}]$ occurs according to the following ionic equations (proposed by S.G. Parshin):

$$
(\text{H}^+) + \text{e}^- + (\text{O}^2^-) + (\text{Fe}^{2+}) = [\text{Fe}] + [\text{O}] + [\text{H}]
$$

(16)

$$
(\text{OH}^-) + \text{e}^- + (\text{Fe}^{2+}) = [\text{FeO}] + [\text{H}]
$$

(17)

In the molten fluoride slags, an ionic reaction binds hydrogen with the formation of anions (OH$^-$) and gaseous compound HF↑. Thus, the formation of anions (OH$^-$), the binding of hydrogen in HF, and formation of network clusters of $\text{AlF}_6^{3-}$ and $\text{AlF}_4^{-}$ anions can energetically hinder the transition of atomic hydrogen into the weld pool and the formation of diffusible hydrogen $[\text{H}]$.

The aim of the research was to develop a gas–slag system for a flux-cored wire for underwater wet welding that has high metallurgical activity and reduces diffusible hydrogen and non-metallic slag inclusions by removing hydrogen and hydroxyl in the vapor–gas bubble atmosphere and increasing the solubility of water vapor in the slag phase.
2. Materials and Methods

Samples of API X70 pipeline steel (CHTPZ, Chelyabinsk, Russia) with bainitic microstructure having dimensions of 300 mm × 200 mm × 21.3 mm was welded underwater in butt and lap joint configurations, as shown in Figure 1.

![Welding samples](image)

Figure 1. Assembly and root pass welding of (a) butt and (b) lap joints.

Mechanized underwater wet welding was performed by divers at a depth of 12 m using a Neptun-4 submersible (Paton Institute of Electric Welding, Kiev, Ukraine). Flux-cored wires were used of type PPS-AN1 (Paton Institute of Electric Welding, Kiev, Ukraine) (TiO₂–Fe₂O₃–MnO–iron powder composition) and PPS-APL2 (Educational Scientific and Technical Center “Svarka”, St. Petersburg, Russia) (TiO₂–CaF₂–Na₃AlF₆–MnO–iron powder composition). The wires had a diameter of 1.6 mm and the rutile electrodes E7014 and UW/CS-1 (Broco, ON, USA) (TiO₂–CaCO₃–SiO₂–Al₂O₃–MnO–iron powder composition) were 3.2 mm in diameter. Welding parameters are shown in Table 1.

| Welding Consumables          | Voltage, V | Current, A | Wire Feed Rate, m/min |
|------------------------------|------------|------------|-----------------------|
| UW/CS-1 electrode            | 37.5–42.5  | 135–175    | -                     |
| PPS-AN1 flux-cored wire      | 37.5–43.5  | 120–300    | 4                     |
| (TiO₂–Fe₂O₃)                 |            |            |                       |
| PPS-APL2 flux-cored wire     | 40–45      | 100–240    | 4                     |
| (TiO₂–CaF₂–Na₃AlF₆)          |            |            |                       |
Mechanical tests were conducted in compliance with GOST 6996–66 using a Super L60 machine (Tinius Olsen, Horsham, PA, USA), a PH450 pendulum impact test system (Walter + Bai AG, Löningen, Switzerland), and an EMCOTEST DuraScan-20 hardness tester (EMCO-TEST PrufmaSchinen GmbH, Kuchl, Austria). The chemical composition was determined with a Bruker Q4 TASMAN optical emission spectrometer (Bruker, Karlsruhe, Germany). A Zeiss Axiocert 200 MAT microscope (Carl Zeiss AG, Oberkochen, Germany) was used to analyze the microstructure, and an ERESCO 42M X-ray unit (GE Sensing and Inspection Technologies GmbH, Ahrensburg, Germany) was used for X-ray testing in compliance with GOST 7512–82. Research of the vapor–gas bubble formation was performed by the vacuum method with a laser system and Phantom VEO 710L high-speed camera (Vision Research, Wayne, NJ, USA) with a frequency of 8000 Hz. Diffusible hydrogen content was determined by the vacuum method according to GOST 34061–2017 (ISO 3690: 2012) using an accelerated method [49] with automatic bead welding in water at the depth of 0.8 m. Thermodynamic calculations were performed using FactSage (CRCT, Montreal, Canada) and Terra (Bauman Moscow State Technical University, Moscow, Russia) and were based on thermodynamic data of individual substances [50].

3. Results and Discussion

Underwater wet welding with a self-shielded flux-cored wire occurs in a vapor–gas bubble formed during dissociation of water. The welding arc consists of a central zone (arc column), a boundary zone around the arc column, and a molecular layer, in which water vapor dissociates. A proposed model of underwater wet welding using flux-cored wire is shown in Figure 2.

![Figure 2](image)

**Figure 2.** Arc model in underwater wet welding (a): 1—arc column; 2—arc boundary; 3—molecular layer of dissociation around the arc boundary; 4—vapor–gas bubble; 5—weld pool; 6—liquid slag; 7—flux-cored wire; 8—drop; (b) vapor–gas bubble shadow photo in flux-cored underwater wet arc welding: CT—contact tube; FCW—flux-cored wire; VGB—vapor–gas bubble; SP—steel plate (proposed by S.G. Parshin).

The formation of a vapor–gas bubble includes several phases: nucleation, volume expansion with the pulsations (or growth), and collapse, as shown in Figure 3.
**Figure 3.** Formation of a vapor–gas bubble: (a) nucleation phase; (b) volume expansion phase; (c) collapse phase.

A detailed model of metallurgical processes in underwater wet welding is shown in Figure 4.

**Figure 4.** Model of metallurgical processes in underwater wet welding in vapor–gas bubble, liquid slag, and liquid weld pool (proposed by S.G. Parshin).
In the molten slag occur the electrochemical interactions between OH⁻ hydroxyl and AlF₆³⁻ and AlF₄⁻ anions with the formation of bonds –F–H–F– and –Al–O–Al–, as shown in Figure 5.

\[
\text{AlF}_6^{3-} = \text{AlF}_4^- + 2\text{F}^- \rightarrow \text{AlF}_4^- + \text{AlF}_4^- = \text{Al}_2\text{F}_7^- + \text{F}^- \rightarrow \text{Al}_2\text{F}_7^- + \text{OH}^- \rightarrow \text{Al}_2\text{OH}_2\text{F}_5^+ + \text{F}^-. \]

**Figure 5.** Electrochemical model of OH hydroxyl binding with the formation of network clusters in the interaction of AlF₄⁻ ions (proposed by S.G. Parshin).

As a result of water dissociation and ionization of molecules, the atmosphere of the vapor–gas bubble consists of a gas mixture of a complex phase composition with high metallurgical activity in reactions with the metal of the molten weld pool, as shown in Figure 6.

\[
\begin{align*}
\text{Me} + \text{OH} &= \text{MeO} + 0.5\text{H}_2 \quad \text{(for Mn, Fe, Co)} \\
2\text{Me} + 3\text{OH} &= \text{Me}_2\text{O}_3 + 1.5\text{H}_2 \quad \text{(for Fe, Cr, Al)} \\
3\text{Fe} + 4\text{OH} &= \text{Fe}_3\text{O}_4 + 2\text{H}_2 \\
\text{Me} + 2\text{OH} &= \text{MeO}_2 + \text{H}_2 \quad \text{(for Ti, Si)}
\end{align*}
\]

**Figure 6.** Molar fraction of components during dissociation of H₂O: (a) up to 5000 K; (b) at 5000–9000 K. Pressure in the system is 0.1 MPa.

Dissociation of water during underwater welding leads to an increase in the hydrogen partial pressure and oxidation of iron and alloying elements Mn, Si, Cr, Ni, etc. The increase in oxidation is dependent on the pressure in the gas system. Particularly active in reactions with liquid metals are the OH hydroxyl group, which is formed in the arc during dissociation of H₂O, and water vapor, which is formed by alloying elements by reactions, as shown in Figure 7.
\[ \text{Me} + \text{H}_2\text{O} = \text{MeO} + \text{H}_2 \text{ (for Mn, Fe)} \quad (22) \]
\[ 2\text{Me} + 3\text{H}_2\text{O} = \text{Me}_2\text{O}_3 + 3\text{H}_2 \text{ (for Fe, Cr, Al)} \quad (23) \]
\[ 3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 \quad (24) \]
\[ \text{Me} + 2\text{H}_2\text{O} = \text{MeO}_2 + 2\text{H}_2 \text{ (for Ti, Si)} \quad (25) \]

Figure 7. Gibbs free energy of metal oxidation reactions: (a) for the OH hydroxyl group; (b) for water vapor $\text{H}_2\text{O}$.

The following elements are particularly active in oxidation reactions with hydroxyl: Al ($\Delta G_{500K} = -1611.9$ kJ), Cr ($\Delta G_{500K} = -1086.5$ kJ), Ti ($\Delta G_{500K} = -911.4$ kJ), Fe in $\text{Fe}_3\text{O}_4$ ($\Delta G_{500K} = -1070$ kJ), and $\text{Fe}_2\text{O}_3$ ($\Delta G_{500K} = -782$ kJ). Resistance to oxidation by water vapor is shown by Ni ($\Delta G_{500K} = +26$ kJ), Cu for $\text{Cu}_2\text{O}$ ($\Delta G_{500K} = +86$ kJ), and Co ($\Delta G_{500K} = +20.3$ kJ).

Thermodynamic modeling of phase equilibria shows that adding 20% $\text{CaF}_2$ and 20% $\text{Na}_3\text{AlF}_6$ into the gas system at 0.1 MPa and at 0.6 MPa leads to a decrease in the partial pressure of H, $\text{H}_2$, and the OH hydroxyl group due to the formation of HF, as shown in Figure 8.

For example, at 3000 K at a pressure of 0.1 MPa with 20% $\text{CaF}_2$ added, the partial pressure of $\text{H}_2$, OH, and O decreases by 9.1, 8.7, and 3.2%, respectively, and with 20% $\text{Na}_3\text{AlF}_6$ added, the partial pressure of $\text{H}_2$, OH, and O decreases by 15.8, 9.8, and 3.16%, respectively. At the pressure of 0.6 MPa at 3000 K, adding 20% $\text{CaF}_2$ reduces the partial pressure of $\text{H}_2$, OH, and O by 7.8, 8.57, and 4.4%, respectively, and adding 20% $\text{Na}_3\text{AlF}_6$ reduces the partial pressure of $\text{H}_2$, OH, and O$_2$ by 15.68, 8.57, and 0.15%, respectively. Adding $\text{CaF}_2$ and $\text{Na}_3\text{AlF}_6$ leads to the formation of HF with a partial pressure of up to 0.01 and 0.058 MPa, respectively, at a system pressure of 0.1 MPa and 0.6 MPa.
Figure 8. Change in partial pressure of components in the equilibrium gas mixture in the vapor–gas bubble at 0.1 MPa (a–c) and at 0.6 MPa (d–f): a,d—100% H₂O; b,e—when adding 20% CaF₂; c,f—when adding 20% Na₃AlF₆.

During heating, the complex fluoride Na₃AlF₆ in the arc dissociates with the formation of NaF and AlF₃. Evaporation and dissociation of CaF₂ and Na₃AlF₆ leads to the formation of NaF, AlF₃, AlF₂,
AlF, and CaF molecules, which reduce the partial pressure of H2 in the vapor-gas bubble and react with H2O and H2 according to reactions shown in Figure 9:

\[
1.5\text{H}_2\text{O} + \text{AlF}_3 = 0.5\text{Al}_2\text{O}_3 + 3\text{HF} \tag{26}
\]

\[
\text{H}_2\text{O} + \text{CaF}_2 = \text{CaO} + 2\text{HF} \tag{27}
\]

\[
0.5\text{H}_2 + \text{NaF} = \text{Na} + \text{HF} \tag{28}
\]

\[
1.5\text{H}_2 + \text{AlF}_3 = \text{Al} + 3\text{HF} \tag{29}
\]

\[
\text{H} + \text{F} = \text{HF} \tag{30}
\]

\[
0.5\text{H}_2 + \text{F} = \text{HF} \tag{31}
\]

**Figure 9.** Gibbs free energy of reactions (26)–(34) of interaction of fluorides and fluorine in a vapor-gas bubble atmosphere at 0.1 MPa (a) and at 0.6 MPa (b).

At high temperatures in the arc, metallurgical reactions occur in the gas phase between the fluorides NaF, AlF₃, AlF₂, and AlF and the oxide TiO₂ with the formation of fluorides TiF₃, TiF₄, and TiF₂, which are highly reactive to H₂O and H₂, for example, in reactions (32)–(34), as shown in Figure 9.

\[
4\text{TiO}_2 + 2\text{Na}_3\text{AlF}_6 = 4\text{TiF}_3 + 3\text{Na}_2\text{O} + \text{Al}_2\text{O}_3 + \text{O}_2 \tag{32}
\]

\[
1.5\text{H}_2\text{O} + \text{TiF}_3 = 0.5\text{Ti}_2\text{O}_3 + 3\text{HF} \tag{33}
\]

\[
1.5\text{H}_2 + \text{TiF}_3 = \text{Ti} + 3\text{HF} \tag{34}
\]

In a TiO₂–Fe₂O₃ slag system with 10% H₂, an increase in the content of the basic oxide Fe₂O₃ to 30% and a decrease in the acidic oxide TiO₂ to 70% results in an increase in the mass fraction of H₂O, especially at the melting temperature of 1700–1750 K. When adding a mixture of fluorides (CaF₂ + Na₃AlF₆) of up to 30% into the TiO₂–CaF₂–Na₃AlF₆ slag system, a sharp decrease occurs in the mass fraction of H₂O in the slag, especially at the melting temperature of 1350–1550 K. A decrease in the H₂O fraction with an increase in the fluorides content can be explained by the formation of HF and TiF₃, which confirms the possibility of reactions (32)–(34) in the slag phase, as shown in Figure 10.
and a decrease in porosity and slag inclusions, as shown in Figure 11.

Testing of flux-cored wires with gas–slag systems TiO$_2$–Fe$_2$O$_3$ and TiO$_2$–CaF$_2$–Na$_3$AlF$_6$ showed that the presence of Fe$_2$O$_3$ can lead to the formation of slag inclusions and penetration defects. Utilization of a TiO$_2$–CaF$_2$–Na$_3$AlF$_6$ gas–slag system provided a higher density of deposited metal and a decrease in porosity and slag inclusions, as shown in Figure 11.

The chemical composition and mechanical properties of the welds are shown in Tables 2 and 3.
Due to oxidation, the content of alloying elements, especially manganese and carbon, significantly decreased in the direction from the root to the cap weld. The lowest transition coefficient for alloying elements was observed when welding with flux-cored wire PPS-AN1, as shown in Figure 12.

![Graph](image)

**Figure 12.** Change in the content of (a) carbon and (b) manganese in different weld zones when welding with the coated electrode UW/CS-1 and flux-cored wires PPS-AN1 and PPS-APL2: RW—root weld; FW—fill weld; CW—cap weld.

Mechanical tests showed that welds made with the flux-cored wire PPS-APL2 have similar characteristics as regards impact toughness, ductility, and hardness as welds made with the coated electrode UW/CS-1; however, the ultimate strength of the welds is 13–15% lower, as shown in Table 3 and in Figure 13.

| Material                     | C     | Si    | Mn    | Ni    | S     | P     |
|------------------------------|-------|-------|-------|-------|-------|-------|
| API X70 steel                | 0.1–0.12 | 0.29–0.31 | 1.7–1.75 | 0.015–0.02 | >0.006 | >0.013 |
| UW/CS-1 electrode            | 0.06–0.1 | 0.3–0.35 | 0.49–0.65 | -     | >0.008 | >0.017 |
| PPS-AN1 flux-cored wire      | 0.04–0.12 | >0.002 | 0.048–0.12 | 1.1–1.47 | >0.013 | >0.018 |
| PPS-APL2 flux-cored wire     | 0.03–0.15 | >0.018 | 0.27–0.52 | 0.8–1.2 | >0.013 | >0.015 |

**Table 2.** Chemical composition of steel and deposited metal in underwater wet welding of API X70 steel, wt.%.  

| Welding Consumables | Yield Strength, MPa | Tensile Strength, MPa | Elongation, % | Impact Toughness, KCV+20, J | Weld Hardness, HV5 |
|---------------------|---------------------|-----------------------|--------------|-----------------|------------------|
| UW/CS-1 electrode   | 440–468             | 498–545               | 6–12         | 68–89           | 165–203          |
| PPS-AN1 flux-cored wire | 323–336         | 371–458               | 2–11.2       | 62–73           | 135–212          |
| PPS-APL2 flux-cored wire | 330–356       | 433–462               | 4–12.6       | 67–98           | 162–200          |

**Table 3.** Mechanical properties of underwater wet welding welds of API X70 steel.
Welds made with the flux-cored wire PPS-AN1 had poorer mechanical characteristics because of the presence of elongated slag inclusions, as shown in Figure 14.

Welds made with the coated electrode UW/CS-1 and flux-cored wire PPS-APL2 had the highest density and a small number of small non-metallic inclusions, as shown in Figures 15 and 16.
This work proposed a model of metallurgical and electrochemical processes in underwater wet welding in a vapor–gas bubble, molten slag, and liquid weld pool based on a thermodynamic modeling for the optimization of the gas–slag system and the improvement of the quality of welds. Thermodynamic modeling and experiments showed that a complex mechanism based on reducing the partial pressure of $H_2O$, $H_2$, $H$, and OH in the atmosphere of the arc and in the vapor–gas bubble and increasing the hydroxyl capacity of the basic slag system can be used to reduce the diffusible hydrogen content and slag inclusions in underwater wet welding of high-strength
steel. This solution is achieved by increasing the metallurgical activity of the gas–slag system in removal of water vapor, hydrogen, and hydroxyl in reactions with the formation of HF and ionic dissolution of water vapor in the form of hydroxyl groups OH in the basic fluorine-containing slag of the TiO₂–CaF₂–Na₃AlF₆ system of the flux-cored wire.

(2) The oxidizing potential of the atmosphere of the arc and the vapor–gas bubble decreases with an increase in fluorides, which improves the transition coefficient of the alloying elements and the density of the deposited metal and reduces the volume of slag inclusions. As a result of using a flux-cored wire with a TiO₂–CaF₂–Na₃AlF₆ system, the average strength and impact toughness of the weld increased by 8 and 22%, respectively, and the diffusible hydrogen content decreased by 21% compared to a flux-cored wire with a TiO₂–Fe₂O₃ system.

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