Thermodynamic Analysis for Tracking the Effect of the Egyptian Zirconium Silicate on the slag properties of low hydrogen Welding Electrodes

A AbdElkarim¹, H M Abd El Aziz², Waleed A Mohrez¹ and H Mashaal¹

¹Nuclear materials Authority, Cairo, Egypt
²Mining and petroleum Dep., faculty of Engineering, Al-Azhar University, Cairo, Egypt

Abstract One of the most common types of welding electrodes, used in welding processes; are the low hydrogen electrode classification; E 7018. This electrode is applied for fabrication most carbon steel alloys, where it used for welding plate works of ships, equipment, tanks, boilers and pressure vessels, steel structures of buildings, bridges as well. One of the most common drawbacks resulting of using of this welding electrode is the difficulty of removing the slag between the deposited passes, which consumes time and money and hence decreasing the quality of welding process also one of the most drawbacks of this type of welding electrode is the rabid burning of coating flux at elevated amperes increase.

This study aimed to suggest rooted solution for these two problems by adding zirconium silicate to the flux recipe. Different percentages of Egyptian zirconium silicate were added to the coating flux recipes of type E7018 where the changes at both weldability and slag removing between deposited passes were noticed at different amperes. By using HSc simulation program of the thermodynamics data and expected phases in slag were studied. Microstructure samples of weld metal were imaged and analyzed, basicity index was calculated, XRF chemical analysis for all slag different samples, were determined. The study concluded that adding 5% of the Egyptian zirconium silicate to the flux clearly improved; the welding properties as well as the ease of slag removal.

Keywords. Zircon, E7018, thermodynamic, black sand and welding electrode

1. Introduction
The continues improvement of flux coated electrode of the type low hydrogen electrodes is indispensable to enhance the performance of welding and its slag removal, where such flux coated type is rich of calcium carbonate or calcium fluoride [1-3] ,the main criteria of success the recipe of low hydrogen electrode ;is to decrease the amount of hydrogen in weld metal ,where this target can be achieved by decreasing the absorption of humidity on the surface of flux coat [4] on the other hand all recipes of low hydrogen type shall keep basicity index not less than “2” to keep the slag mobility and weld deposition smooth as much as applicable [5] ,all applicators and manufacturers seeking to select electrodes, which possesses such potentiality of slag removal between passes to decrease the time of welding deposition especially in hot passes filling at large thicknesses of base metal .

Weld bead contour or profile of weld deposition can be affected by the slag chemistry and its physical properties one of the main parameters which affecting on weld profile is the high temperature slag , which called at some texts as “refractory slag “, which provides an advantage of rabid solidification before the weld metal to be solidified, forming a mold rounded wall that holds the molten metal in confined place
[6-10] Zirconium and hafnium compounds are widely used in today’s technology to achieve such refractory slag and hence achieving such rabid solidification of the slag[11-14].

In this research we used a different recipes using different zirconium oxide percentage at the flux coating, and hence the basicity index of each recipe was changed as well ,where we used percentage of zirconium oxide 1,3,5,7,9 % by weight of flux coating ,all phases of flux dissociated phases were calculated by thermodynamic calculation method of “HSC chemistry 5 “to find the optimum condition and the most appropriate zirconium oxide percentage, which shall be added to the recipe to achieve most viable slag removal.

We also investigated the mechanical properties of the weld metal to track any variation of the designed mechanical properties of such electrode with such variation in the slag chemistry.

All investigations have been achieved to track and analysis the phases which formed in the slag; by XRF and chemical analysis, also soundness tests by non-destructive methods were done by radiographic.

2. Experimental work
2.1. Thermodynamic Calculations

Before proceeding adding zirconium silicate ore in the form of zirconium silicate to welding electrode flux coat, a comprehensive calculation was carried out in order to have a pre-estimation of the materials balance conditions.

Computer software for simulation all reactants and materials balance called” HSC chemistry-5” was used to calculate the thermodynamic parameters at different reaction temperatures. The calculations showed that it is possible to dissociate ZrSiO₄ to ZrO₂ and SiO₂ in accordance to the following equation:

\[ \text{ZrSiO}_4 \rightarrow \text{ZrO}_2 + \text{SiO}_2 \]

As shown in table (1) thermodynamic data for previous equation it is noticed that the negativity of free energy value (Delta G) started at temperature 1200 C, which means that the dissociation temperature of ZrSiO₄ will dissociate spontaneously to direction of formation both ZrO₂ and SiO₂.

To ensure that All of dissociated ZrO₂ quantity, which came from added zirconia to the flux coat, will be directly moved to the slag phase and was neither reduced to Zr metal and nor interfered inside the weld metal.

The thermodynamic calculations for the three expected reduction reactions of ZrO₂ with metals; Fe (existed in form of iron powder), Mn (in form of ferromanganese) and Si (in form of ferrosilicon) were done according to equations and the results were shown in tables (2,3 and 4)

\[ \text{ZrO}_2 + \text{Si} = \text{Zr} + \text{SiO}_2 \]

\[ \text{ZrO}_2 + 2\text{Fe} = \text{Zr} + 2\text{FeO} \]

\[ \text{ZrO}_2 + 2\text{Mn} = \text{Zr} + 2\text{MnO} \]

From tabulated data in table (2, 3 and 4) can deduce that \( \Delta G \) at temperature range from 0 to 2000 °C is positively value ,which means that the reduction of ZrO₂ by previous three reducing metals ( Si,Fe and Mn) will not be done and all quantity of ZrO₂ will directly orient into slag and weld metal will not be interfered byZrO₂.

By Using HSC chemistry-5 program the prediction phases of slag with changed adding quantity of ZrSiO₄ to flux recipe as 2,4 and 6% from weight, were done and shown in figures 1:a, B and C.
Table 1. Thermodynamic data of the dissociation reactions

| T (°C) | ΔH (kJ) | ΔS (J/K) | ΔG (kJ) | K       | Log(K) |
|--------|---------|----------|---------|---------|--------|
| 0.000  | 12.590  | 7.637    | 10.504  | 9.797E-003 | -2.009 |
| 200.000| 13.033  | 8.835    | 8.853   | 1.053E-001 | -0.977 |
| 400.000| 13.210  | 9.148    | 7.052   | 2.836E-001 | -0.547 |
| 600.000| 14.519  | 10.765   | 5.119   | 4.940E-001 | -0.306 |
| 800.000| 14.062  | 10.292   | 3.017   | 7.131E-001 | -0.147 |
| 1000.000| 16.022 | 12.106   | 0.609   | 9.441E-001 | -0.025 |
| 1200.000| 24.754 | 18.161   | -12.000 | 1.177E+000 | 0.071 |
| 1400.000| 24.875 | 18.237   | -5.638  | 1.500E+000 | 0.176 |
| 1600.000| 25.116 | 18.373   | -9.298  | 1.817E+000 | 0.259 |
| 1800.000| 35.905 | 23.774   | -13.383 | 2.174E+000 | 0.337 |
| 2000.000| 38.556 | 24.995   | -18.261 | 2.628E+000 | 0.420 |

Table 2. Thermodynamic calculation for possibility of ZrO₂ reduction by Si.

| T (°C) | ΔH (kJ) | ΔS (J/K) | ΔG (kJ) | K       | Log(K) |
|--------|---------|----------|---------|---------|--------|
| 0.000  | 189.576 | 11.901   | 186.326 | 2.322E-036 | -35.634 |
| 200.000| 188.597 | 9.172    | 184.257 | 4.537E-021 | -20.343 |
| 400.000| 188.332 | 8.651    | 182.508 | 6.865E-015 | -14.163 |
| 600.000| 189.841 | 10.520   | 180.655 | 1.555E-011 | -10.808 |
| 800.000| 189.713 | 10.386   | 178.567 | 2.031E-009 | -8.692 |
| 1000.000| 195.036 | 15.196   | 175.690 | 6.183E-008 | -7.659 |
| 1200.000| 185.382 | 8.465    | 172.911 | 7.386E-007 | -6.132 |
| 1400.000| 184.710 | 8.036    | 171.265 | 4.495E-006 | -5.347 |
| 1600.000| 134.585 | 21.719   | 175.268 | 1.294E-005 | -4.888 |
| 1800.000| 145.660 | -16.175  | 179.192 | 3.053E-005 | -4.515 |
| 2000.000| 170.831 | -4.390   | 180.811 | 6.995E-005 | -4.155 |
Table 3. Thermodynamic calculation for possibility of ZrO2 reduction by Fe

| T (°C) | ΔH (kJ) | ΔS (J/K) | ΔG (kJ) | K            | Log(K)  |
|--------|---------|----------|---------|--------------|---------|
| 0.000  | 565.228 | 47.546   | 552.241 | 2.431E+106   | -105.614|
| 200.000| 568.244 | 56.144   | 541.679 | 1.566E+060   | -59.805 |
| 400.000| 569.447 | 58.350   | 530.169 | 7.192E+042   | -41.143 |
| 600.000| 568.497 | 57.195   | 518.558 | 9.454E-042   | -31.024 |
| 800.000| 563.382 | 51.992   | 507.586 | 1.957E-025   | -24.708 |
| 1000.000| 564.266| 52.799   | 497.044 | 4.033E-021   | -20.394 |
| 1200.000| 556.519| 47.461   | 486.601 | 5.556E-018   | -17.255 |
| 1400.000| 604.154| 76.408   | 476.313 | 1.345E-015   | -14.871 |
| 1600.000| 577.646| 61.798   | 461.890 | 1.314E-013   | -12.881 |
| 1800.000| 577.746| 61.847   | 449.529 | 4.708E-012   | -11.327 |
| 2000.000| 600.083| 72.326   | 435.676 | 9.723E-011   | -10.012 |

Table 4. Thermodynamic calculation for possibility of ZrO2 reduction by Mn

| T (°C) | ΔH (kJ) | ΔS (J/K) | ΔG (kJ) | K            | Log(K)  |
|--------|---------|----------|---------|--------------|---------|
| 0.000  | 329.690 | 43.179   | 317.895 | 1.598E+061   | -60.796 |
| 200.000| 330.035 | 44.372   | 309.041 | 7.582E+035   | -34.120 |
| 400.000| 329.260 | 43.040   | 300.288 | 4.972E+024   | -23.303 |
| 600.000| 327.926 | 41.318   | 291.849 | 3.461E+018   | -17.461 |
| 800.000| 321.701 | 34.950   | 284.194 | 1.465E+014   | -13.834 |
| 1000.000| 323.249| 36.388   | 276.922 | 4.340E+012   | -11.362 |
| 1200.000| 302.811| 21.877   | 270.583 | 2.541E+010   | -9.595  |
| 1400.000| 272.359| 1.928    | 269.134 | 3.955E+009   | -8.403  |
| 1600.000| 268.301| -0.367   | 268.988 | 3.151E+008   | -7.502  |
| 1800.000| 264.768| -2.161   | 269.248 | 1.643E+007   | -6.784  |
| 2000.000| 371.618| 48.409   | 261.777 | 9.641E+007   | -6.016  |

From figure 1 we can observed that all ZrSiO4 approximately dissociated to ZrO2 and a part of it was reacted with CaO, which existed in the molten slag phase and formed CaZrO3 compound, the melting point of phase CaZrO3 (2340 °C) is lower than Melting point of ZrO2 (2710 °C), which means that the formation of ZrO2 compound in molten slag phase is better than CaZrO3, where it leads to preventing an early burning of the electrode. From the figs we can concluded that adding 4% ZrSiO4 to slag is the best conditions, where the presence of ZrO2 with more quantity than CaZrO3. The increasing of ZrSiO4 percent to 6% will lead to an increase percent of CaZrO3 phase and decreasing ZrO2 and hence leads to early burning to stick electrode and deteriorate the welding performance and increasing the consumption of welding electrodes.

From thermodynamic calculation we can conclude that: -
1- All ZrSiO$_4$ will be dissociating at 1000 to 1200°C.
2- All ZrSiO$_4$ will not reduce to Zr metal and all quantity will be slag former.
3- The increasing of ZrSiO$_4$ higher than 5% is not useful.

Figure 1. Prediction phases of slag with adding (a: 2%, b: 4% and C: 6%) ZrSiO$_4$
3. Experimental and Methodology Procedure

3.1 Manufacturing of welding electrode
The experimental work and methodology represents on the materials processing and balance to produce different recipes such as investigated from thermodynamic data with different percentage of zirconium silicate with percentage of 1,3,5,7% by weight. The raw materials of zirconium silicate is a commercial grade with a purity of 99% with using screen analysis for controlling mesh size up to -500 micron from Rosetta black sand, Egypt. We used two routes of mixing one by dry process for one hour by dry mixer rotating sparely with 100 RPM, then followed by dry mixing inside wet dryer for 30 minutes with adding bindery material as potassium silicate to make adhesion of the flux coat, then followed by high pressure extrusion process to coat the flux on the surface of core wire. Then the extruded green electrodes were aerated at open air yard for 48 hours to solidify the flux coat locally by increasing its cohesion and adhesion, then the electrodes packed inside electric furnace to temperature 350°C for six hours to elaborate the flux coat from the absorbed humidity.

3.1. Welding process
After drying and packing of the welding electrode we selected our samples of test with three diameters 3.25, 4, and 5 mm with flux coat diameter up to then we conducted deposition the weld metal with weaving technique.

3.2 Testing and analysis
Investigation by XRF analysis for the sample were done, a cooperation with fusion company for welding electrode a five recipe of flux with their contents were done the percent of adding ZrSiO₄ were changed as following in table 5 below.

| No of recipe | % ZrSiO₄ |
|--------------|-----------|
| 1            | without   |
| 2            | 1         |
| 3            | 3         |
| 4            | 5         |
| 5            | 7         |

After the production of electrodes the performance test with a professional welder were done for 5 samples and XRF of slag phase for each sample was done to investigate the percentage of zirconia in the slag, mechanical and chemical test of the weld metal for each sample also was done to investigate if there any negative or positive impacts in the mechanical properties of the weld metal soundness test for the best sample were done.

4. Results and Discussions

4.1 Zircon ore Analysis
Run of mine sample of the zircon ore was analyzed to investigate and assure from the purity and percentage of zirconia in the ore by XRF device, the analysis is as resulted at the tabulated data in table 6, where “zirconia “ZrO₂ and HfO₂% showed that it is up to 67% and silicate SiO₂% up to 32.6%.
4.2. Analysis of Slag and Metal Phases and welding performance
The results of analyse of this stage is divided into mechanical test of weld metal for each test sample, chemical analyses for both metal and slag phase and the monitoring of welding performance, welding amperage required for each test sample and slag removal as well on the other hand.

4.3. Welding performance and amperage required.
It was noticed that the test samples, showed various welding performance and variant amperage values with changing the percentage of added zirconium ore, when no addition of zirconium for sample No 1 it show immoderate welding performance and amperage ranging from 130,170,200 for diameters 3.25, 4, 5 mm respectively and showed severe difficulty of slag removal after each pass due to physical adhesion between slag and metal interface required mechanical gauging and brushing to clean the passes from the slag formed, whereas ,when an increase of the percentage of zircon ore from 1 ,3,5,7 % to samples 2,3,4,5 respectively it was noticed that the amperage required for burning increased from (130,170,200 amperes) with diameters 3.25, 4, 5 mm respectively to (140,180,210amperes) for sample 2 and (150,190,230 amperes) for sample 3 and (160,210,250 amperes) for sample 4,and (160,210,250 amperes) for sample 5 as shown in table 7 and was noticed also that there was clear enhancement of slag removal after each pass with increasing the percentage of zirconium directly proportional .

4.3.1. Chemical Analysis of Metal and Slag Phases.
The chemical analysis of metal and slag phase was conducted where the analysis of slag phase for each test sample has been investigated to track the phase of zirconia, which dissociated from zirconium silicate.
The results in table 8 showed that the sample No 1 without any addition of zirconium silicate gives a zirconia up to 0.025 which may be come from other gangue minerals, but when increasing the zirconium

Table 6. XRF analysis of Zircon concentrate

| ZrO₂ | HfO₂ | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | P₂O₃ | Ignition loss at 1025 |
|------|------|------|------|-------|-------|-----|-----|------|----------------------|
| 65.47| 1.32 | 32.58| 0.05 | 0.06  | 0.05  | 0.03| 0.05| 0.13 | 0.14                 |

Where the most easy slag removal has been investigated in the sample number 5 with percentage of zirconium 5% as shown in figure 2 where an increase of zirconium as high temperature refractor mineral worked as mold wall contributed positively to prevent any physical and chemical bonding between slag and weld metal phase at the reaction interface ,this result is not only impacted to the welding performance positively but also impacted economically during the productivity of welding ,where such result will decrease the time of finishing the deposition especially at the large thicknesses.

Table 7. Maximum Ampere for electrode burning

| Sample No. | ZrSiO₄ % | Max. ampere, A |
|------------|----------|----------------|
|            |          | 3.25 mm Electrode diameter | 4.00 mm Electrode diameter | 5.00 mm Electrode diameter |
| 1          | 0        | 130            | 170            | 200            |
| 2          | 1        | 140            | 180            | 210            |
| 3          | 3        | 150            | 190            | 230            |
| 4          | 5        | 160            | 210            | 250            |
| 5          | 7        | 160            | 210            | 250            |
silicate at samples 2, 3, 4, 5 showed appearance of zirconia with values; (0.67, 2.08, 3.45, 4.88%) respectively, whereas the balance of silicate impacted at the silicon oxide which appears with percentage (22.08, 22.99, 23.91, 25.8%) for such samples 2, 3, 4, 5 respectively as shown in tables 9. The dissociation of zirconium silicate to zirconia and the percentage of each phase is agreed with the thermodynamic data which conducted by HSC chemistry 5.

![Sample 1](image1)
![Sample 2](image2)
![Sample 3](image3)
![Sample 4](image4)
![Sample 5](image5)

**Figure 2. Slag and welding profile**

**Table 8. Chemical analysis for weld metal**

| Sample No. | ZrSiO$_4$ % | C  | Mn  | Si  | P   | S   |
|------------|--------------|----|-----|-----|-----|-----|
| 1          | 0            | 0.56 | 1.24 | 0.514 | 0.018 | 0.013 |
| 2          | 1            | 0.55 | 1.26 | 0.567 | 0.019 | 0.011 |
| 3          | 3            | 0.61 | 1.16 | 0.48  | 0.016 | 0.013 |
| 4          | 5            | 0.57 | 1.19 | 0.436 | 0.018 | 0.014 |
| 5          | 7            | 0.64 | 1.22 | 0.472 | 0.020 | 0.016 |

The weld metal analysis of the sample number 1 with comparison of samples 2, 3, 4, 5 showed no considerable changes in chemical analysis where this proofed that there was not any estimated mobility of zirconium silicate or it dissociated fraction towards the weld metal and almost was oriented to the slag phase.
Table 9. Chemical analysis for slag

| Sample No. | ZrSiO₄% | Chemical composition % |
|------------|---------|------------------------|
|            |         | CaO       | SiO₂     | Al₂O₃    | TiO₂     | Fe₂O₃    | MnO      | ZrO₂     | K₂O      | Na₂O     |
| 1          | 0       | 53.52     | 21.11    | 1.55     | 10.76    | 4.29     | 5.12     | 0.025    | 2.11     | 1.48     |
| 2          | 1       | 52.12     | 22.08    | 1.58     | 10.56    | 4.14     | 5.88     | 0.67     | 1.99     | 0.96     |
| 3          | 3       | 49.24     | 22.99    | 1.6      | 10.44    | 4.11     | 5.78     | 2.08     | 1.94     | 1.01     |
| 4          | 5       | 47.13     | 23.91    | 1.77     | 10.58    | 4.08     | 5.68     | 3.45     | 1.98     | 1.4      |
| 5          | 7       | 45.66     | 25.8     | 1.53     | 10.28    | 4.17     | 5.56     | 4.88     | 1.28     | 0.78     |

4.3.2. Mechanical analysis of weld metal.

The mechanical test of the weld metal for each test sample shown in table 10 was conducted to assure and investigate the impact of addition the zirconium silicate, where the chemical analysis which confirmed that there was no any considerable change in the chemical analysis between sample No 1 and other samples with variable percentage of zirconium silicate the addition of zirconium didn’t affected on the deposition and fluidity of the weld metal which didn’t impacted negatively to the mechanical analysis of the weld metal ,the ultimate tensile strength of sample No1,2,3,4,5 was 540,543,537,544,543 MPa respectively which means that there was no any considerable effect of addition zirconium silicate on the mechanical test of weld metal.

Table 10. Tensile test of weld metal

| Sample No. | ZrSiO₄% | Yield strength N/mm² | Ultimate tensile strength N/mm² | Elongation % |
|------------|---------|----------------------|---------------------------------|--------------|
| 1          | 0       | 429                  | 540                             | 34           |
| 2          | 1       | 430                  | 543                             | 34           |
| 3          | 3       | 422                  | 537                             | 32           |
| 4          | 5       | 433                  | 544                             | 33           |
| 5          | 7       | 428                  | 543                             | 34           |

5. Conclusion.

This research targeted the study of the effect of adding zirconium ore from Egyptian run of mine, without any preparation or processing, except grinding and sizing, the study has been accomplished by two routes; one is basic and other is secondary for assurance and confirmation the first one ,the first rout is conducting thermodynamic analysis for showing and tracking the phases of dissociation the zirconium silicate in which forms have been dissociated and how these forms behaves with other additives. Thermodynamic analysis showed that zirconium silicate has been dissociated to zirconia (ZrO₂) at temperature 1200°C with Delta G of -2 KJ and continued spontaneously for dissociation to temperature up to 2000°C with Delta G of -18.261 KJ. Also, thermodynamic analysis confirmed that the optimum quantity of zirconium silicate which shall be added is not more than 4 -5 % where any increase of quantity will lead to form calcium zirconate (CaZrO₃) on the credit balance of zirconia. Thermodynamic analysis revealed any suspicious of the probability that zirconium dioxide (ZrO₂) may be reduced by manganese, Silicon or iron , which already existed at the recipe at the form of Ferro manganese and Ferro silicon where Gibbs’s free energy calculations showed that there is no any negativity of the reduction reaction can be occurred with an elevated temperature up to 2000°C.
The chemical analyses of the slag phases of test samples showed that zircon phases have been oriented to the slag and contributed effectively as high temperature refractory material prevented any chemical or physical bonding between slag and metal phases, which led to prompt, easy slag removal after each pass deposited. The chemical analysis also confirmed that there is no any evidence of zircon or its phases entered to weld metal. The mechanical test of the weld metal showed that there is no any positive or negative effect on the mechanical value of ultimate tensile test of test samples and all their value was average as 540MPa.

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