Effect of microstructure and alloying elements distribution on welding quality of Zircaloy-4

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Abstract. In order to understanding the appearance of the abnormal welding line during the CANDU fuel element end plug welding process, the analysis on the microstructure and the alloying elements distribution of three different batches of Zircaloy-4 rods, named as A753, B592 and C744, was carried out in the present study. The microstructure and localized composition of the alloys were studied by optical microscopy, X-ray diffractometer (XRD), high-resolution transmission electron microscopy (HRTEM) and energy disperse spectroscopy (EDS). The results showed that there was no obvious difference among the three specimens. However, it was found that there appeared etch pits in the middle area of A753 batch samples. And the grain size of welding qualified C744 batch sample was greater than the un-qualified samples of A753 and B592. According to HRTEM and EDS results, the second phase particles in the Zircaloy-4 were Zr(Fe, Cr)₂ phase with the Hexagonal Close-Packed (HCP) structure. The matrix belonged to α-Zr phase with the Hexagonal Close-Packed (HCP) structure. The second phase particles distributed inside the grains and at the grain boundaries of the three batches of the alloys. The size of the second phase particles in qualified sample C744 was around 200nm with the elements of Zr, Fe and Cr. However the size of the second phase particles in the un-qualified samples B592 and A753 was about 100nm, in which the elements of Fe and Cr could not be detected or only trace amount of Fe could be detected for part of the second phase particles. Therefore it may be concluded that the grain size, the second phase size and composition are the main factors to affect the welding quality of the alloy.

Keywords: Zircaloy-4, second phase particles, welding quality

1. Introduction
In the manufacture process of nuclear fuel elements, the Zirconium based alloys such as Zircaloy-2 and Zircaloy-4 are widely used as the structural material and fuel cladding material for the excellent performance in corrosion resistance and mechanical properties [1,2]. As it is known that the preferable comprehensive performance has a direct relationship with the microstructure. In order to provide the reference for the improvement of technology, many literatures [3-10] study the microstructure of Zirconium based alloy prepared under different conditions. The microstructure analysis carried out with transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray diffractometer (XRD), neutron diffraction and the electron backscatter diffraction (EBSD). Among these characterizing techniques, the TEM and XRD is mature and widely used in the microstructure analysis. For example, reference [3] studies the relationship between microstructure and corrosion behaviour of Zr-Nb alloy using the TEM and XRD. Reference [4] studies the microstructure of Zircaloy-4 tube under the condition of hot extrusion, cold rolling and annealing with TEM. At present
the Zircaloy-4 is widely used as the end caps in Pressurized Heavy Water Reactor (PHWR) fuel elements. The abnormal welding line appeared in the detection of the end plug welding products of individual batches, the product will be judged to be substandard. In order to find out whether there are some differences between the qualified batch products and the unqualified batch products, the microstructure and composition of Zircaloy-4 are analysed by OM, HRTEM and EDS. It can provide the reference for the better application of Zircaloy-4 in the production.

2. Experimental

The material used in this study is Zircaloy-4 made in Canada. Three batches of Zircaloy-4 were selected and numbered C744, B592 and A753 respectively. The welding products were qualified of C744 batch. The welding products were unqualified of A753 and B592 batches. The chemical composition of the alloy is given in table 1. In order to find out the differences between three batches Zircaloy-4, Firstly, the macro-structure and the grain size were observed and measured by OM. The phase was tested by the XRD. The microstructure was studied by the F30 TecnaiG2 high resolution transmission electron microscopy. And EDS is chosen to analyse the composition of the second phase particles and matrix.

Table 1. Chemical composition of Zircaloy-4 (wt.%).

| Element | Sn  | Fe  | Cr  | Fe+Cr | Zr    |
|---------|-----|-----|-----|-------|-------|
| Content | 1.20~1.70 | 0.18~0.24 | 0.13 | 0.18~0.38 | Balance |

3. Results and Analysis

3.1. Optical metallographic study of Zircaloy-4

The macroscopic metallographic were carried out on the A753, B592 and C744 batches samples. Five samples for each batch were detected. There was no difference in the metallographic structure of the three batches samples, which was shown in figure 1. When the samples were observed at high magnification it was found that the samples of A753 batch was different from C744 and B592, as shown in figure 2. There were many pits on the surface of the sample, three of the five samples appeared this phenomenon, and the reason remains to be further studied.

Figure 1. Microscopic metallographic photos of three batches of Zircaloy-4.

Figure 2. High magnification metallographic photos of three batches of Zircaloy-4.
The grain size of the three batches samples was analyzed by the cut-off point method. Statistical analysis of the data of grain size was shown in table 2. It can be seen that the grain size of C744 batch samples was larger than that of B592 and A753 batch samples. The grain is shown in figure 3.

**Table 2. Statistical data of grain size of three batches samples.**

| Sample number | Grain size (μm) | average(μm) |
|---------------|----------------|-------------|
| A753-1        | 9.48           |             |
| A753-2        | 9.51           | 9.24        |
| A753-3        | 8.72           |             |
| B592-1        | 9.33           |             |
| B592-2        | 8.64           | 8.95        |
| B592-3        | 8.90           |             |
| C744-1        | 9.20           |             |
| C744-2        | 10.01          | 9.94        |
| C744-3        | 10.63          |             |

**Figure 3.** Grain size photographs of three batches samples.

### 3.2. Phase analysis of Zircaloy-4

Two samples of each batch were carried out on phase by XRD, as shown in figure 4. According to the query results of the PDF card the phase is α-Zr. The phase of three batches of Zircaloy-4 is the same.

**Figure 4.** Diffraction patterns of different batches of Zircaloy-4.

### 3.3. Analysis of microstructure and composition of Zircaloy-4

The thin film samples were examined and analysed with high-resolution transmission electron microscopy. Figure 5 shows the TEM micrographs and EDS spectrum of Zircaloy-4 samples. From the results, it can be found that the second phase particles were distributed into the matrix and the
main composition was Zr, Fe and Cr. The main composition of the matrix was Zr. Figure 6 presents the HRTEM and Fourier transform picture of the second phase particles and matrix.

Table 3. Statistics table for EDS data of the second phase particles and matrix in figure 5.

| Position | Element | wt.% | at.% | Position | Element | wt.% | at.% |
|----------|---------|------|------|----------|---------|------|------|
| TEM5-1   | Cr      | 14.79| 19.76| TEM5-2   | Cr      | 0.00 | 0.00 |
|          | Fe      | 31.90| 39.66|          | Fe      | 0.23 | 0.38 |
|          | Zr      | 55.28| 40.56|          | Zr      | 99.75| 99.6 |

Figure 5. TEM micrographs and EDS spectrum of B592 batch Zircaloy-4 samples.

Figure 6. TEM micrographs, HRTEM and Fourier transform results of Zircaloy-4 samples.
Transform the HRTEM picture of the second phase particles and matrix with the Fourier transform, the statistics of the second phase particles were obtained from figure 6(a) \((d_1=0.1279\text{nm}, \ d_2=0.2569\text{nm})\). The results were in accordance with the PDF #42-1289 results\((d=0.1279\text{nm}, \ d=0.2504\text{nm})\). According to the EDS results from table 3, the second phase particles were composed of Zr, Fe and Cr. And the reference \([11]\) shows that the phase between \(n(\text{Fe})/n(\text{Cr})=1.55 \sim 3.45\) is \(\text{Zr(Fe,Cr)}_2\). According to the comprehensive analysis, the second phase particles in figure 6 are \(\text{ZrFe}_1\text{Cr}_0.5\) with the Hexagonal Close-Packed (HCP) structure. And the lattice constant is \(a=5.007\), \(c=8.193\). The computation results from figure 6(b) \((d_1=0.1859\text{nm}, \ d_2=0.2462\text{nm})\) were identical to the PDF #65-3366 statistics \((d=0.1894\text{nm}, \ d=0.2459\text{nm})\). And the main composition of the matrix was Zr, the matrix in the figure 6 is \(\alpha\text{-Zr}\) with the Hexagonal Close-Packed (HCP) structure.

![Figure 7. STEM micrographs and EDS spectrum of B592 batch Zircaloy-4.](image)

![Table 4. Statistics table for EDS data of the second particles and matrix in figure 7.](table)

| Position | Element | wt.% | at.% | Position | Element | wt.% | at.% |
|----------|---------|------|------|----------|---------|------|------|
| STEM 7-1 | C       | 0.01 | 0.08 | STEM 7-2 | C       | 0.00 | 0.00 |
|          | O       | 0.23 | 1.21 |          | O       | 0.04 | 0.27 |
|          | Cr      | 4.39 | 6.94 |          | Cr      | 0.00 | 0.00 |
|          | Fe      | 10.26| 15.11|          | Fe      | 0.00 | 0.00 |
|          | Zr      | 85.07| 76.62|          | Zr      | 99.94| 99.71|
| STEM 7-3 | C       | 0.13 | 1.03 | STEM 7-4 | C       | 0.21 | 1.59 |
|          | Cr      | 0.00 | 0.00 |         | Cr      | 0.00 | 0.00 |
|          | Fe      | 0.00 | 0.00 |  (matrix)| Fe      | 0.00 | 0.00 |
|          | Zr      | 99.86| 98.96|         | Zr      | 99.78| 98.40|

Figure 7 shows the STEM and EDS results of the TEM samples of Zircaloy-4. From the STEM and EDS results listed in table 4, the second phase particles distributed at the grain boundaries and inside the grains of B592 batch. The second phase particles were round, ellipse and square with the size in the range of 100 nm. The main composition of the second phase particles was Zr, Fe and Cr, the contents of Fe and Cr varies a lot: \(n(\text{Fe})/n(\text{Cr})=1.55 \sim 3.45\). According to the research \([12-14]\), the Fourier transform spot and EDS statistical analysis indicate that the second phase particles were the
Zr(Fe, Cr)₂ with the Hexagonal Close-Packed (HCP) structure. The composition of the matrix was mainly Zr and there existed micro-scale of Fe in some location. The matrix is α-Zr phase with the Hexagonal Close-Packed (HCP) structure. The content of Fe and Cr of the point 2 and point 3 was zero in the scanning transmission photographs.

Figure 8 is TEM micrographs of the C744 batch Zircaloy-4. The composition of the second phase particles was Zr, Fe and Cr.

![Figure 8. TEM micrographs and EDS spectrum of C744 batch Zircaloy-4.](image)

| Position | Element | wt.% | at.% |
|----------|---------|------|------|
| TEM8-1   | O       | 0.31 | 1.37 |
|          | Cr      | 15.17| 19.95|
|          | Fe      | 32.38| 39.62|
|          | Zr      | 52.11| 39.04|
| TEM8-2   | O       | 1.36 | 5.52 |
|          | Cr      | 22.05| 27.34|
|          | Fe      | 29.07| 33.56|
|          | Zr      | 47.48| 33.55|

Table 5. Statistics table for EDS data of the second particles in figure 8.

Transform the HRTEM picture of the second phase particles and matrix with the Fourier transform, the statistics of the second phase particles were obtained from figure 9(a) \( (d_1=0.2479\text{nm}, d_2=0.1349\text{nm}, d_3=0.1553\text{nm}) \). The results were in accordance with the PDF #42-1289 results \( (d=0.2504\text{nm}, d=0.1364\text{nm}, d=0.1553\text{nm}) \). According to the EDS results from Table 5, the second phase particles were composed of Zr, Fe and Cr. And the reference[11] shows that the phase between \( n(\text{Fe})/n(\text{Cr})=1.22\sim2.37 \) is Zr(Fe, Cr)₂. According to the comprehensive analysis, the second phase particles in figure 9 were ZrFe₁.₅Cr₀.₅ with the Hexagonal Close-Packed (HCP) structure. And the lattice constant is \( a=5.007, c=8.193 \). The computation results from figure 9(b) \( (d_1=0.1610\text{nm}, d_2=0.2756\text{nm}) \) were identical to the PDF #65-3366 statistics\( (d_1=0.1615\text{nm}, d_2=0.2798\text{nm}) \). And the main composition of the matrix was Zr, the matrix in the figure 9 was α-Zr with the Hexagonal Close-Packed (HCP) structure.
Figure 9. TEM micrographs, HRTEM and Fourier transform results of C744 batch Zircaloy-4.

Figure 10 is STEM micrographs of the C744 batch Zircaloy-4. The composition of the second phase particles was Zr, Fe and Cr.

Figure 10. STEM micrographs and EDS spectrum of C744 batch Zircaloy-4.
From the above photos and EDS results it can be found the second phase particles distributed at the grain boundaries and inside the grain in the Zircaloy-4 of C744 batch. The second phase particles were round, ellipse and square with the size around 200nm. The main composition of the second phase particles was Zr, Fe and Cr. The contents of Fe and Cr varies a lot: \(n(\text{Fe})/n(\text{Cr})=1.22 \sim 2.37\). According to the reference, the Fourier transform spot and EDS statistical analysis indicate that the second phase particles were the \(\text{Zr(Fe, Cr)}_2\) with the Hexagonal Close-Packed (HCP) structure. The composition of the matrix is mainly Zr.

Figure 11 and figure 12 is TEM and STEM micrographs of the A753 batch Zircaloy-4. It can be seen the second phase particles distributed at the grain boundaries and inside the grain. The size of the second phase particles was around 100nm with the main composition of Zr, Fe and Cr. Individual second phase particles contained only Fe. The content of the Cr was zero, which is showed in table 8.

| Position | Element | wt.%  | at.%  | Position | Element | wt.%  | at.%  |
|---------|---------|-------|-------|---------|---------|-------|-------|
| STEM    | Cr      | 16.14 | 20.97 | STEM    | Cr      | 5.58  | 8.72  |
| 10-1    | Fe      | 33.17 | 40.12 | 10-2    | Fe      | 12.85 | 18.69 |
|         | Zr      | 50.29 | 37.25 |         | Zr      | 81.54 | 72.56 |

From the above photos and EDS results it can be found the second phase particles distributed at the grain boundaries and inside the grain in the Zircaloy-4 of C744 batch. The second phase particles were round, ellipse and square with the size around 200nm. The main composition of the second phase particles was Zr, Fe and Cr. The contents of Fe and Cr varies a lot: \(n(\text{Fe})/n(\text{Cr})=1.22 \sim 2.37\). According to the reference, the Fourier transform spot and EDS statistical analysis indicate that the second phase particles were the \(\text{Zr(Fe, Cr)}_2\) with the Hexagonal Close-Packed (HCP) structure. The composition of the matrix is mainly Zr.

![Figure 11](image1.png)

**Figure 11.** TEM micrographs, HRTEM and Fourier transform results of A753 batch Zircaloy-4.
### Table 7. Statistics table for EDS data of the second particles in figure 11.

| Position | Element | wt.% | at.% | Position | Element | wt.% | at.% |
|----------|---------|------|------|----------|---------|------|------|
| TEM 11-1 | O       | 0.00 | 0.00 | TEM 11-1 | O       | 1.42 | 5.87 |
|          | Cr      | 17.06| 21.73|          | Cr      | 16.75| 21.30|
|          | Fe      | 36.26| 46.56|          | Fe      | 29.43| 34.84|
|          | Zr      | 43.66| 31.69|          | Zr      | 52.39| 37.97|
| TEM 11-3 | O       | 3.66 | 10.43|          | Cr      | 14.41| 12.63|
|          | Fe      | 26.19| 21.38|          | Zr      | 48.28| 24.13|

### Figure 12. STEM micrographs of A753 batch Zircaloy-4.

### Table 8. Statistics table for EDS data of the second particles in figure 12.

| Position | Element | wt.% | at.% | Position | Element | wt.% | at.% |
|----------|---------|------|------|----------|---------|------|------|
| STEM 12-1 | C       | 0.00 | 0.00 | STEM 12-2 | Fe      | 0.20 | 0.32 |
|          | Cr      | 12.62| 17.75|          | Zr      | 63.36| 50.80|
|          | Fe      | 24.00| 31.43|          | C       | 0.65 | 4.67 |
|          | Zr      | 63.36| 50.80|          | C       | 0.93 | 6.68 |
| STEM 12-3 | Cr      | 0.82 | 1.35 | STEM 12-4 | Fe      | 0.01 | 0.02 |
|          | Fe      | 2.69 | 4.13 |          | Zr      | 95.82| 89.23|
|          | Zr      | 95.82| 89.23|          | C       | 0.46 | 3.20 |
| STEM 12-5 | Cr      | 0.04 | 0.06 | STEM 12-6 | Fe      | 12.08| 17.02|
|          | Fe      | 11.17| 16.57|          | Zr      | 63.67| 51.15|
|          | Zr      | 88.31| 80.15|          | Zr      | 63.67| 51.15|
Figure 13. TEM micrographs, HRTEM and Fourier transform results of A753 batch Zircaloy-4.

Transform the HRTEM picture of the second phase particles and matrix with the Fourier transform, the statistics of the second phase particles were obtained from figure 13(a) ($d_1=0.2105\text{nm}$, $d_2=0.1252\text{nm}$). The results were in accordance with the PDF #42-1289 results ($d=0.2136\text{nm}$, $d=0.1252\text{nm}$). According to the EDS results from table7, the second phase particles were composed of Zr, Fe and Cr. And the reference shows that the phase between $n(\text{Fe})/n(\text{Cr})=1.22\sim 3.45$ is $\text{Zr(Fe, Cr)}_2$. According to the comprehensive analysis, the second phase particles in figure 13 were $\text{ZrFe}_{1.5}\text{Cr}_{0.5}$ with the Hexagonal Close-Packed (HCP) structure. And the lattice constant is $a=5.007\text{nm}$, $c=8.193\text{nm}$. The computation results from figure 13(b) ($d_1=0.2553\text{nm}$, $d_2=0.2826\text{nm}$) were identical to the PDF #65-3366 statistics ($d=0.2553\text{nm}$, $d=0.2798\text{nm}$). And the main composition of the matrix was Zr, the matrix in the figure 13 was $\alpha$-Zr with the Hexagonal Close-Packd (HCP) structure.

The microstructure and composition were studied of three batches Zircaloy-4. It can be found that the second phase particles distributed at the grain boundaries and inside the grain in the Zircaloy-4. The size of the second phase particles was around 100-200nm with the main composition of Zr, Fe and Cr. The contents of Fe and Cr varies a lot: $n(\text{Fe})/n(\text{Cr})=1.22\sim 3.45$. According to the reference, the Fourier transform spot and EDS statistical analysis indicate that the second phase particles were the $\text{Zr(Fe, Cr)}_2$ with the Hexagonal Close-Packed (HCP) structure. The composition of the matrix was mainly Zr.

In the above analysis it can be also found that individual second phase particles contained only Fe. The content of the Cr was zero or the content of Fe and Cr were zero according to EDS in the figure 7 and figure 12. There is no phenomenon in the second phase particles of the figure 10. The composition of the second phase particles contained Fe and Cr. This was the different between the three batches Zircaloy-4.

4. Conclusion

There is no obvious difference observed by the macro metallographic analysis among the three batches Zircaloy-4. However the etch pits in the middle area of the A753 batch samples have been observed. The grain size of C744 batch samples is greater than the samples A753 and B592 batches. The phase of three batches Zircaloy-4 is $\alpha$-Zr by XRD.
The Zircaloy-4 matrix was $\alpha$-Zr phase with the HCP structure. The second phase particles was Zr(Fe, Cr)$_2$ with the HCP structure. The second phase particles distribute at grain boundaries and inside the grains.

The size of the second phase particles in qualified sample C744 is about 200nm with the elements of Zr, Fe and Cr; and the sizes of the second phase particles in the un-qualified samples B592 and A753 are about 100nm, in which the elements of Fe and Cr could not be detected or only trace amount of Fe could be detected for part of the second phase particles.

Therefore it may be concluded that the grain size, the size and composition of the second phase are the main factors to affect the welding quality of the alloy.

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