Task 1: Alloy Fabrication and Characterization

This task included manufacturing model alloys to investigate the corrosion mechanism of Zr alloys. The model alloys can be categorized into various groups: Zr-Sn, Zr-Nb, Zr-Nb-Sn, Zr-Fe-Cr, Zr-Cr-Fe, Zr-Cu-Mo and a last group of reference alloys (crystal bar, sponge Zr and Zircaloy-4). Additional model alloys with higher alloying element content were manufactured by KAERI in 2004. The chemical composition of the model alloys tested in this project is summarized in Table 1.1 and 1.2.

The model alloys were prepared by arc melting. The arc-melted buttons were re-melted at least 4 times to promote chemical homogeneity. A typical arc-melted button measures about 70 mm in diameter and 10 mm in thickness, and weighs about 400 g. The arc-melted ingots were beta-solution treated at 1050^{o}C for 30 min in a vacuum furnace, hot-rolled after pre-heating at 580 to 720C for 10 min and cold-rolled three times to a final thickness of 0.8 mm. Between the rolling steps, the cold-rolled sheets were intermediate-annealed at a temperature of 580 to 720^{o}C depending on the alloy system. Specimens for corrosion testing, 25 by 20 by 0.8 mm in size, were cut from the manufactured strip, mechanically ground up to 1200 grit SiC paper, and then pickled in a solution of 5 vol.% HF, 45 vol.% HNO_3 and 50 vol.% H_2O.

Table 1.1. Target chemical composition of the original model alloys.

Group	Composition (wt.%)	Process temperature
Zr-Sn	Zr-0.2Sn, Zr-0.4Sn Zr-0.8Sn, Zr-1.2Sn	580^{o}C
Zr-Nb	Zr-0.2Nb, Zr-0.4Nb Zr-1.0Nb, Zr-1.5Nb Zr-2.5Nb	650^{o}C
Zr-Sn-Nb	Zr-0.4Sn-0.2Nb Zr-0.4Sn-0.4Nb	650^{o}C
Zr-Fe-Cr	Zr-0.2Fe-0.1Cr (L) Zr-0.2Fe-0.1Cr (H) Zr-0.2Fe-0.1Cr (L) Zr-0.2Fe-0.1Cr (H)	L: 580^{o}C H: 720^{o}C
Zr-Cr-Fe	Zr-0.5Cr Zr-0.5Cr-0.2Fe Zr-1.0Cr Zr-1.0Cr-0.2Fe	650^{o}C
Zr-Cu-Mo	Zr-0.5Cu Zr-0.5Cu-0.5Mo Zr-1.0Cu Zr-1.0Cu-0.5Mo	580^{o}C
Reference	Zr sponge Crystal bar Zr Zircaloy-4	580^{o}C 580^{o}C 720^{o}C

Table 1.2. Target chemical composition of the additional model alloys.

Group	Composition (wt.%)	Process temperature
1.0Fe	Zr-1.0Fe	650^{o}C
	Zr-1.0Fe-0.5Cr	650^{o}C
0.6Fe	Zr-0.6Fe	650^{o}C
	Zr-0.6Fe-0.3Cr	650^{o}C
	Zr-0.6Fe-0.3Mo	650^{o}C
	Zr-0.6Fe-0.6Nb	580^{o}C
1.0Cr	Zr-1.0Cr-0.5Fe	650^{o}C
	Zr-1.0Cr-0.5Mo	650^{o}C

Grain Size of as-fabricated model alloys

The as-fabricated alloys were examined using polarized light microscopy in reflection mode to measure the average grain size. The alloys show a homogeneous predominantly equiaxed grain microstructure, as would be expected from a recrystallizing heat treatment. The measured grain sizes are reported in Table 1-. Micrographs of these alloys are shown in Appendix A.

Table 1-3: Grain size.

Alloy Designation	Composition	Grain Size (microns)	Stdev
11	Zr-0.2Fe-0.1Cr L	9.67	2.65
12	Zr-0.2Fe-0.1Cr H	14.51	3.41
41	Sponge Zr	11.27	2.03
42	Crystal bar Zr	15.37	2.83
43	Zircaloy-4	14.19	2.88

The grain size measured in the Zr-0.2Fe-0.1Cr alloys annealed at high temperature is bigger than the same sample annealed at low temperature, as expected. The largest grain size of all is observed in crystal bar Zr, which is in agreement with the fact that this is the lowest alloying element content alloy, since alloying elements tend to slow down grain growth.

Hardness of Model Alloys

To obtain a rough measure of the mechanical properties of the fabricated alloys, Vickers micro-hardness measurements were taken. Samples were cut and mounted in epoxy and tested in a LECO V-100-C1 hardness tester for a 10 second period under a 1000 g load. The results show that, with the exception of the crystal bar Zr, all alloys tested exhibited hardnesses in the range 140-170, with small variations within series. The series with higher alloying contents had slightly higher hardness values than those ones with lower alloying element content. This indicates that the alloys have similar mechanical characteristics (with the exception of crystal bar Zr).

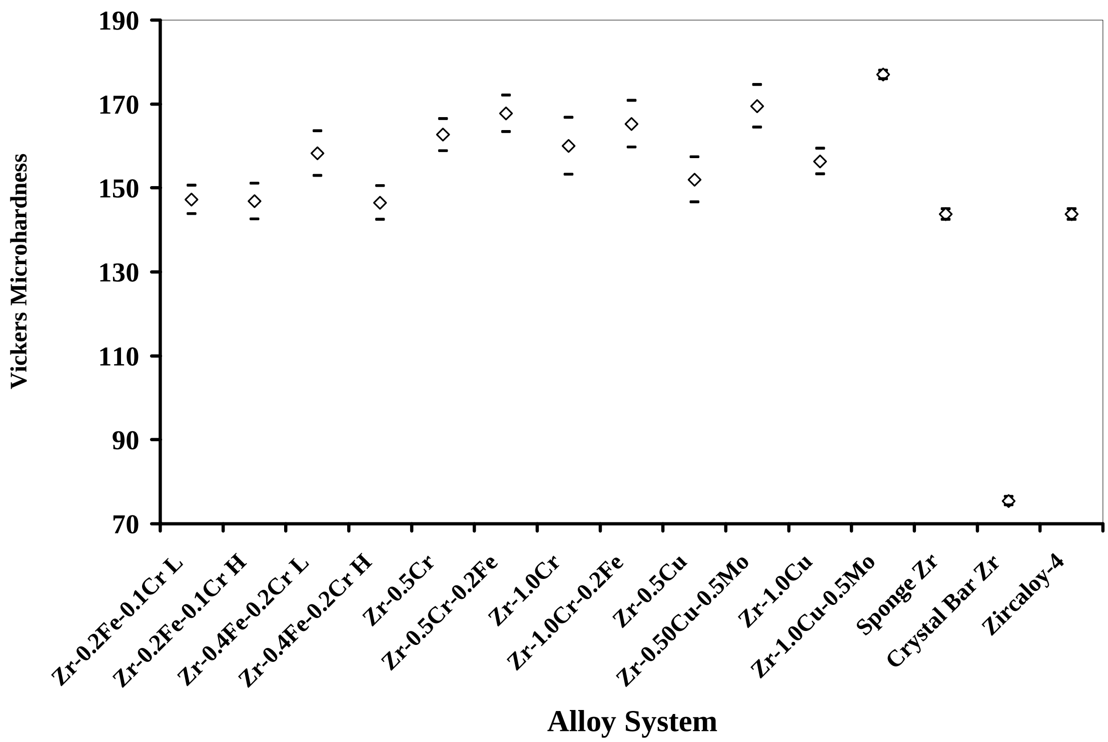

Figure 1-1: Vickers micro-hardness for all the model alloys investigated.

Texture Measurements of as fabricated alloys

Basal diffraction pole figures of as-fabricated alloys were collected and the results are shown in Appendix F. The Kearns factors (defined as the fraction of resolved basal poles aligned along a particular macroscopic direction [1]) were calculated from the inverse pole figure of the alloys, and are shown in Table 1.4. The calculated f_N (fraction of basal poles along normal direction) ranges from 0.59 to 0.64, again with the exception of crystal bar Zr which exhibits a f_N =0.51. This value is similar to reported values of f_N for as-fabricated Zr components.

Table 1-4: f_N measured for the model alloys.

Alloy	***Texture index***
14 - Zr-0.4Fe-0.2Cr H	0.62
21 - Zr-0.5Cr	0.59
22 - Zr-0.5Cr-0.2Fe	0.62
23 - Zr-1.0Cr	0.62
24 - Zr-1.0Cr-0.2Fe	0.69
33 - Zr-1.0Cu	0.63
34 - Zr-1.0Cu-0.5Mo	0.63
41 - Sponge Zr	0.64
42- Crystal Bar Zr	0.51
43- Zircaloy-4	0.68

Thus the texture, hardness and grain size of the alloys is similar. Given that homogeneous and similar microstructures were obtained, it is possible to isolate the other variables as composition differences and investigate their impact on the corrosion behavior of the alloys, as is the objective of this study.

Characterization of second-phase particles (SPP)

The alloys prepared and used in this study and their target chemical compositions are listed in Table 1-5. The actual compositions were measured and did not vary from the target composition by more than 10% (e.g. Zr1.0Fe, could vary by ± 0.1Fe, to Zr0.9Fe or Zr1.1.Fe). The main groups contained alloys that form second phase particles (Zr-Fe-Cr alloys, Zr-Cr-Fe alloys, Zr-Cu-Mo) and alloys that form extensive solid solutions in alpha-Zr, (Zr-Nb, Zr-Sn and Zr-Nb-Sn) in addition to pure Zr and Zircaloy-4.
The as-fabricated model alloys were characterized using synchrotron radiation X-ray diffraction to identify second phases present. One example of such an examination is shown in Figure 1.2, where the x-ray intensity is plotted versus two theta angle acquired using an x-ray energy of 17 keV, for the examination of the alloys Zr-0.4Fe-0.2Cr and Zr-0.2Fe-0.1Cr, processed at 580°C (indicated as L for low temperature heat treatment) and 720°C (indicated H for high temperature heat treatment). The vertical scale is logarithmic to highlight in greater detail the small second phase peaks, which comprise only a small fraction of the total sample volume. The experiments were run the APS synchrotron facility where the combination of the high photon flux and the low background permits detection of small diffraction peaks. Second phase particles having

volume fractions as low as 0.1 to 0.2% can be detected, as the ones expected for the alloy systems investigated in this project. Figure **Error! Reference source not found.** illustrates these capabilities.

The alloys were characterized using synchrotron radiation X-ray as described in chapter 2 and the target precipitate structures and sizes were observed. The types of precipitates identified and their approximate size and volume fraction are also shown in Table 1-6. It is apparent from the table that synchrotron radiation allows a level of characterization of the metallic alloy microstructure that can help highlight the specific role of individual alloy features on the corrosion process.

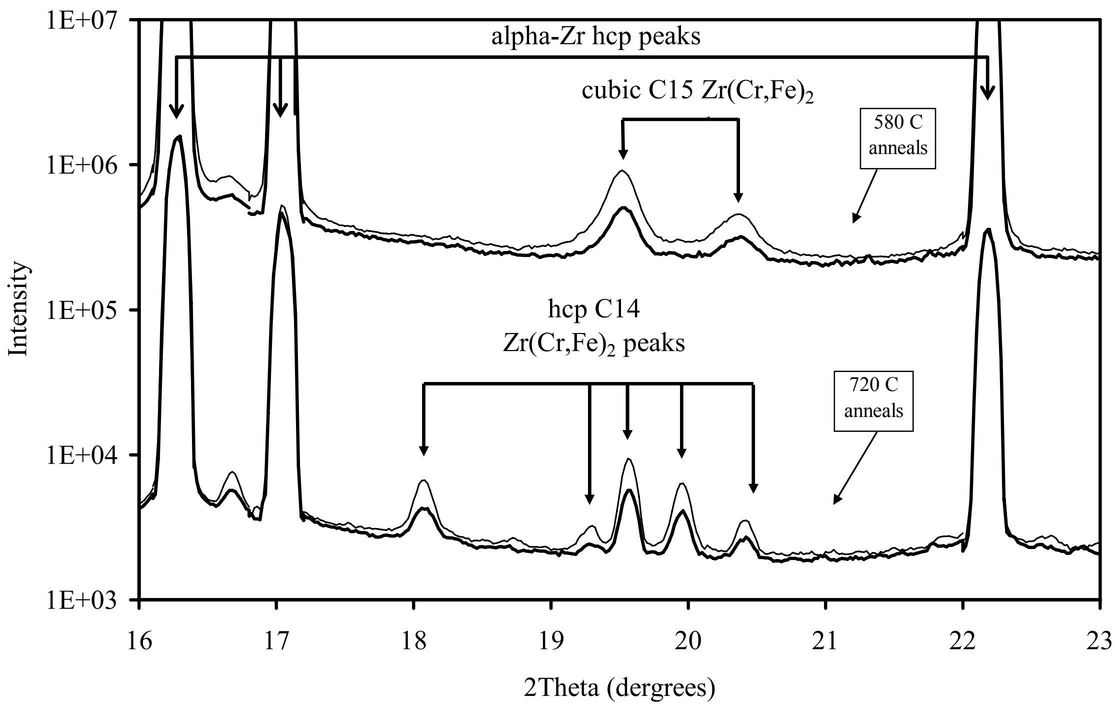

Figure 1.2: Diffracted intensity versus two-theta angle (logarithmic scale) for two Zr-Fe-Cr alloys (Zr-0.2Fe-0.1Cr and Zr-0.4Fe-0.2Cr) processed at two different temperatures (580 and 720^{o}C) obtained with synchrotron radiation for the purpose of identification of second phase particles phases present in the alloy.

The precipitates volume fractions were calculated assuming that all the present elements have precipitated out, which is consistent with the findings from the diffraction patterns, where the peaks heights for alloys having similar alloying contents were very close.

The instrumental line broadening was measured using a diffraction pattern collected from a NIST LaB_6 standard (Standard Reference Material 660a Lanthanum Hexaboride Powder). The instrumental broadening was measured to be 0.05 degrees in 2θ at 9.5

keV. After subtracting the instrumental peak broadening, the FWHM (full width at half maximum) of the diffraction peaks was calculated as seen on Equation:

$$FHWM_{2\theta} = \sqrt{FWHM^{2}_{Observed} - FWHM^{2}_{LaB_6}} \tag{1-1}$$

Table 1.5 : Characteristics of the model alloys.

Alloy system	Composition (wt.%)	Precipitate Characteristics		
		Crystal Structure	Size (nm)	Volume Fraction
Zr-Nb	Zr-0.2, 0.4, 1.0, 1.5, 2.5Nb	hcp $Zr(Nb,Fe)_2$, bcc β-Nb and orthor. Zr_3Fe	75-110	Increases as Nb content increases (0-2.3%)
Zr-Fe-Cr	Zr-0.4Fe-0.2Cr and Zr-0.2Fe-0.1Cr (two processing temperatures: 580 °C (L) and 720 °C (H))	Cubic and hex. $Zr(Cr,Fe)_2$	35-107	~1%
Zr-Cr-Fe	Zr0.5Cr, Zr-0.5Cr-0.2Fe, Zr-1.0Cr, Zr-1.0Cr-0.2Fe	Cubic $ZrCr_2$ and cubic $Zr(Cr,Fe)_2$	40-60	~1-1.5%
Zr-Cu-Mo	Zr-0.5Cu, Zr-0.5Cu-0.5Mo Zr-1.0Cu, Zr-1.0Cu-0.5Mo	Tet. Zr_2Cu and cubic $ZrMo_2$ when Mo present	> 100	~0.5-2%
Zr-Sn-Nb	Zr-0.4Sn-0.2Nb, 0.4Sn-0.4Nb	no precipitates	N/A	N/A
Zr-Sn	Zr-0.2, 0.4, 0.8, 1.2 Nb	no precipitates	N/A	N/A
Reference Alloys	Sponge Zr, Crystal bar Zr, Zircaloy-4	no precipitates for Zr hcp C14 $Zr(Cr,Fe)_2$ for Zircaloy-4	80	~0.5 for Zircaloy-4

Similar characterization was performed for all the alloys studied. All alloys considered for this study formed second-phase precipitates with the exception of Zr-0.2Nb and Zr-0.4Nb alloys, which have a Nb concentration below the solubility limit in α-Zr. The types of second phase precipitates were: (i) of the C14 hcp $Zr(Cr,Fe)_2$ type in the ZrFeCr and ZrCrFe alloys (with the exception of the low temperature processed materials which exhibited cubic C15 type Laves phase precipitates of similar composition) , (ii) bcc β-Nb and hcp $(Zr,Nb)Fe_2$ precipitates in the Zr-Nb alloys (Fe is an impurity in these alloys at 100-600 ppm) (iii) cubic C15 $ZrCu_2$ and hcp C14 $ZrMo_2$ type in the ZrCuMo alloys and (iv) the usual precipitates in Zircaloy-4. No precipitates were detected in either sponge or crystal bar Zr, and the detection limit is estimated at <0.1%. The different processing temperatures in the ZrFeCr alloys created alloys with small and large precipitates and the two compositions gave different volume fractions.

References:

[1] J. J. Kearns and C. R. Woods, J. Nucl. Mater., vol. 20, (1966), 241.