

Time-resolved x-ray diffraction and electrical resistance measurements of structural phase transitions in zirconium

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Abstract. We have designed a portable pressure controller module to tune compression rates and maximum pressures attainable in a standard gas-membrane diamond anvil cell (DAC). During preliminary experiments, performed on zirconium (Zr) metal sample, pressure jumps of up to 80 GPa were systematically obtained in less than 0.2s (resulting in compression rate of few GPa/s up to more than 400 GPa/s). In-situ x-ray diffraction and electrical resistance measurements were performed simultaneously during this rapid pressure increase to provide the first time resolved data on $\alpha \rightarrow \omega \rightarrow \beta$ structural evolution in Zr at high pressures. Direct control of compression rates and peak pressures, which can be held for prolonged time, allows for investigation of structural evolution and kinetics of structural phase transitions of materials under previously unexplored compression rate-pressure conditions that bridge traditional static and shock/dynamic experimental platforms.

1. Introduction

Over the last ~50 years, the advancement of diamond anvil cell (DAC) high pressure devices and associated techniques have occurred almost in parallel with evolution of new synchrotron radiation facilities. Today, the most advanced 3rd and 4th generation x-ray facilities continue to offer further increases in x-ray beam brightness, higher flux, improved on-sample beam focus, etc. These advancements offer new opportunities for high pressure (P) and temperature (T) DAC experiments, such as the ability to conduct time-resolved monochromatic x-ray diffraction (XRD) experiments [1]. In addition to improved x-ray beam properties, performing time-resolved XRD measurements also requires systematic control of compression rates with DAC and the ability to couple (i.e. timing, synchronization, etc.) all of the experimental apparatuses. Here we will discuss some of our recent efforts in developing simultaneous high-pressure and variable-compression rate DAC capability, and subsequent work done in coupling this new capability with simultaneous *in situ* XRD and electrical resistance measurements for investigating structural stability of transition metal zirconium (Zr).



1.1. Motivation for development of high pressure-variable compression rate technique

Time-resolved measurements of structural evolution are essential for further improving our understanding of materials behaviour at extreme P-T conditions. The majority of currently available experimental P-T data on materials has been obtained with static high-pressure platforms (i.e. DAC and large volume press devices) or dynamic/shock compression techniques. The two experimental techniques, static and shock, offer a glimpse into material behaviour at two extreme ends of the strain rate spectrum. For example, standard static techniques provide P-T snapshots of crystal structure and crystallographic unit cell volume data at discrete P-T points. Shock compression, on the other hand, is used to generate high P-T states rapidly (\sim ps) and provides insights into material behaviour under high compression/strain rates ($>10^5 \text{ s}^{-1}$), with P-T intertwined on the Hugoniot [2]. Time-resolved XRD experiments with DAC offer a possibility to investigate material behaviour at intermediate strain rate conditions, which bridge the gap between the static ($<10^{-3} \text{ s}^{-1}$) and shock ($>10^5 \text{ s}^{-1}$) techniques. Exploring the strain rate gap region is crucial for measuring the kinetics of phase transitions, investigating structural stability/transformations as a function of compression rate, determining structural evolution and transition pathways, etc. It has been previously demonstrated that intermediate compression rates can be achieved over small pressure range (\sim few GPa) by impacting an opposed-anvil setup with a low-velocity projectile [3] or by attaching electromechanical piezoelectric actuators to a DAC (d-DAC) [4]. Herein we demonstrate that high compression rates can be achieved over a much broader pressure range using a standard gas-membrane DAC.

1.2. Structural stability of zirconium at high pressures

Zirconium, like the other group IVa transition metals titanium (Ti) and hafnium (Hf), has an hcp crystal structure at room P-T. With pressure increase, a transition from hcp, also referred to as α phase, to another hexagonal structure with three atoms per unit cell (ω) is observed in Zr, Ti, and Hf [5]. The martensitic $\alpha \rightarrow \omega$ transition in Zr occurs at ~ 4 to 8 GPa, depending on loading condition, impurity concentration, and sample texture [6], and is then followed by another transition to a bcc (β) crystal structure at ~ 31 GPa [7]. Zr has been investigated in some detail at high-pressure, including static high-pressure XRD-DAC measurements [5-7], high strain rate shock measurements [8], as well as simultaneous XRD-electrical resistance measurements with a large volume press [9]. The breadth of available experimental data from both static and shock experiments, coupled with having a fairly large x-ray scattering cross section, makes Zr an ideal sample for our variable-compression rate and time-resolved measurements.

2. Experimental details and test measurements

In all experiments, a polycrystalline high purity Zr sample was used [6, 8, 10]. Experiments were performed at beamline 16-ID-B at HPCAT, APS [11] and at Extreme Conditions Beamline (ECB) at PETRA III, DESY [1].

2.1. High pressure-variable compression rate setup

As mentioned, Singh [3] and Evans *et al.* [4] have demonstrated that high compression rates can be achieved over a small, few GPa, pressure range using an opposed anvil type setup. In designing our high-pressure variable-compression rate platform, shown in figure 1, we aimed to meet a couple of goals: the new capability has to be able to produce high compression rates over a much broader pressure range, so that multiple phase transitions (as in case of Zr) can be investigated in a single experiment, and experimental platform has to be portable, easy to use, and easily adaptable with various diagnostic probes, such as XRD, optical spectroscopy, etc. Further details regarding various components of our high compression rate setup will be presented in a separate publication. The main components, shown in figure 1, include: an input gas supply; an intermediate buffer that can be filled to a given pressure and is located close to the DAC; sitting between the buffer and DAC is an electric solenoid valve, that can be triggered (i.e. opened-closed) on a *ms* time scale; and a standard gas-membrane equipped DAC. Gas-membrane equipped DACs, which allow for easy and remote control

of pressure increase on the sample, are in standard use at most beamlines today [12]. The basic principle of our compression system relies on use of the intermediate components (buffer and solenoid valve) for controlling gas release to the membrane on a short time scale (\sim ms). Final pressure increase and compression rate can be systematically controlled by increasing/decreasing gas pressure in the buffer and varying the solenoid trigger time – i.e. longer triggering of solenoid valve results in a large gas pressure increase in the membrane, while increase/decrease of the buffer pressure controls rate of gas delivery to the membrane. Ultimately pressure on the sample is also controlled by culet diameter of the diamond anvils and ductility of the gasket used in the experiment.

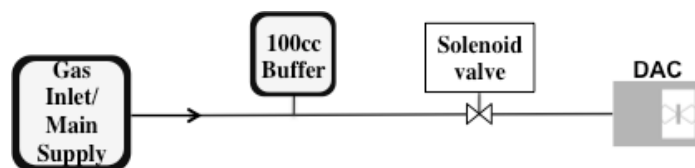


Figure 1. Experimental setup for achieving high pressure-variable compression rates with DAC.

2.2. X-ray diffraction and electrical resistance measurements in high compression rate experiments

Our high-pressure variable-compression rate controller may be used with any gas-membrane equipped DAC and can be easily introduced at any synchrotron beamline. We have demonstrated the new capability at both ECB-DESY and at HPCAT-APS beamlines. Using monochromatic x-ray radiation, XRD patterns were collected *in situ* with either PILATUS 100K or XRD1621 PerkinElmer detector. X-ray detectors used in our experiments allowed for XRD measurements on the order of 0.067 s/spectra (this includes both exposure and readout time per spectra). In the earliest test measurements, only XRD was used to establish feasibility of achieving high-pressure variable-compression rates with our setup. As the compression rate was increased, in addition to XRD, designer diamond anvils [13] were also implemented for simultaneous *in situ* electrical resistance measurements. Using the combination of Keithley 6221 constant current source and 2182A nano-voltmeter [14] sensitive (\sim m Ω) changes in electrical resistance can be measured at a rate of 100 reading/s. Simultaneous collection of XRD-electrical resistance data can then be correlated to further provide information on structural behaviour of materials at high P-T.

3. Results and discussion

Our experiments evolved in the following manner: initial test measurements were performed to confirm the versatility of the response of gas-membrane, we then made improvement to achieve higher compression rates, and finally, coupling/synchronization of pressure control-XRD-electrical resistance measurements was achieved.

In our first test measurement, the membrane pressure was increased from 0 to 55 bar at rate of 40 bar/minute, and XRD measurements were continuously collected at 0.067 s/spectra during the pressure increase. Over 3000 XRD spectra collected while gas pressure is continuously supplied to the membrane. From XRD spectra we were able to determine that the resulting sample pressure increased from \sim 0.1 GPa up to \sim 41 GPa at a rate of \sim 0.5 GPa/s. Over this pressure range we observed first *in situ* $\alpha \rightarrow \omega \rightarrow \beta$ structural evolution in Zr – in figure 2 we show a sampling of spectra collected as Zr undergoes $\alpha \rightarrow \omega$ transition starting at \sim 4 GPa and followed by onset of $\omega \rightarrow \beta$ transition at \sim 31 GPa.

Following the initial test measurement, we performed a number of subsequent experiments with varying gas pressure in the buffer and solenoid triggering times – some of the results are shown in table 1. As can be seen in the table, a range of pressure jump conditions can be achieved. In each experiment XRD measurements were being recorded *in situ* and continuously during gas pressure increase. From XRD data we determine that pressure jump (ΔP) between initial and final pressure occurs in a span of two XRD spectra, corresponding to \sim 0.13 s. In experiments 1-4, with fastest XRD measurements of 0.067 s/spectra, we are able to resolve crystal structure of Zr before and after

pressure jump, obviously this work would benefit from additional increase in x-ray beam performance. In the meantime we have also introduced designer anvil electrical resistance measurement to further probe changes during pressure increase.

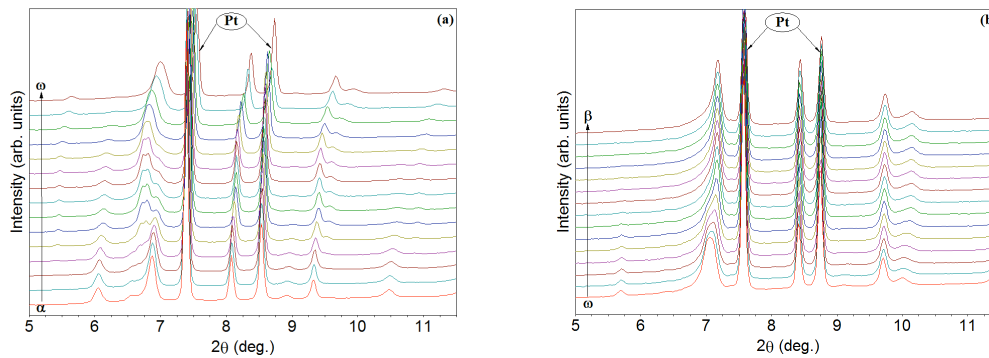


Figure 2. XRD spectra collected in situ showing evolution of (a) $\alpha \rightarrow \omega$ transition and (b) $\omega \rightarrow \beta$ transition, in Zr at high pressure. Peaks from platinum (Pt) pressure marker are labelled.

Table 1. Summary of some of the high pressure-variable compression rate experiments performed. Exp. 1-4 were carried out using diamond anvils having a 300 μm culet diameter, while a designer anvil with 250 μm culet was used in exp. 5. Pressure jump, ΔP , between initial and final pressure occurs in ~ 0.13 s (see text for additional information).

Experiment #	Buffer pressure (bar) / Trigger time (s)	Initial sample pressure (GPa)	Final sample pressure (GPa)	ΔP (GPa)
1	55.3 / 0.073	0.3	29.7	29.4
2	55.2 / 0.083	2.1	34.1	32.0
3	69.3 / 0.031	0.1	38.2	38.1
4	68.9 / 0.055	0.1	46.4	46.3
5	103.4 / 0.055	1.1	81.9	80.8

In experiment 5, XRD and electrical resistance measurements were synchronized to obtain data on structural stability of Zr during fast pressure increase. Using a multi-channel Tektronix DPO TDS5104B oscilloscope, triggering of our gas release system, PILATUS x-ray detector signal, and electrical resistance measurements, were all recorded on a single device, figure 3. The three signals shown in figure 3 correspond to open-close electrical output sent by PILATUS x-ray detector during exposure and readout cycle, input electrical signal triggering of gas release solenoid valve (as shown in figure 2), and resulting electrical resistance change in Zr sample. Oscilloscope can be triggered to initiate data recording by any of the input signals and provides a direct method of time-stamping experimental measurements and correlating structural and electrical resistance changes in the sample. As demonstrated in figure 3, in experiment 5 the start of data recording ($t=0$) on the scope was triggered by the electrical signal sent to open the solenoid valve (shown in red). From XRD data: first spectra shows the sample at 1.1 GPa in α phase; second spectra, following triggering of the solenoid valve and gas release to the membrane, shows a “smeared” diffraction signal as the pressure increases from 1.1 to ~ 71.3 GPa; subsequent, third spectra, and all spectra thereafter show sample at 81.9 GPa and in β phase. Based on XRD data alone there is missing information as to what occurs to the sample as the pressure jumps from 1.1 to 81.9 GPa. However, the corresponding electrical resistance data

over this pressure range clearly shows two kinks, and based on our supplementary measurements as well as work done by Tangea et al. [9], we know that these correspond to $\alpha \rightarrow \omega$ and $\omega \rightarrow \beta$ transition.

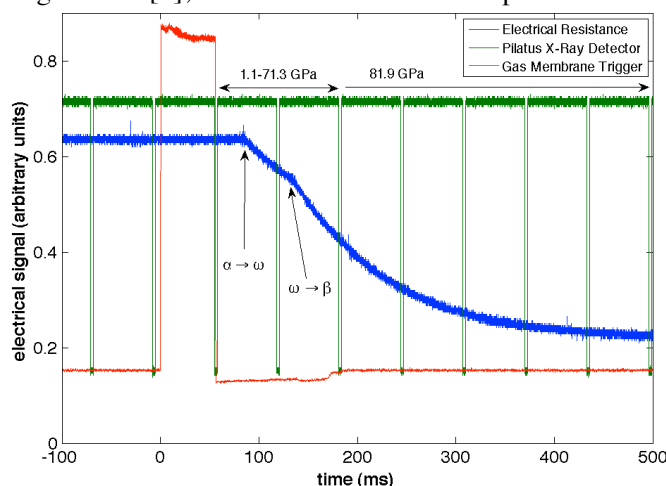


Figure 3. Simultaneous recording of x-ray detector signal (green), gas membrane trigger (red), and electrical resistance of Zr (blue).

4. Conclusions

In summary, we show that DAC can be used to achieve a broad range of pressure and compression rate conditions. Our high pressure-variable compression rate technique, which is portable and easy to use, adds another powerful method for studying material properties at extreme P-T conditions. Furthermore, we also demonstrate a direct method for coupling various experimental probes and synchronization of measurements for investigating structural stability of materials as a function of pressure and compression rate.

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