

Parametric Rietveld Refinement Applied to *In Situ* Diffraction Studies

M.J. Styles^a, D.P. Riley^{a,b}, I.C. Madsen^c and E.H. Kisi^d

^a Dept. Mechanical Engineering, School of Engineering, The University of Melbourne, Victoria 3010, Australia.

^b Australian Institute of Nuclear Science and Engineering, Locked Bag 2001 Kirrawee DC, New South Wales 2232, Australia.

^c CSIRO Process Science and Engineering, Clayton, Victoria 3168, Australia.

^d School of Engineering, The University of Newcastle, New South Wales 2308, Australia.

Parametric Rietveld refinement is an analysis technique that allows physical models to be incorporated into the analysis of sequential powder diffraction patterns. The technique can be used to stabilise the refinement procedure and provides a means of evaluating, and further refining, the physical models selected. Application of both the traditional sequential and newer parametric analysis techniques is discussed, using a time-resolved neutron diffraction study of $M_{n+1}AX_n$ phase synthesis as an example.

1. Introduction

In situ powder diffraction is a technique particularly conducive to the development of physical models of material behaviour, as data concerning material structure can be collected as a function of the processing or environmental variable of interest. Traditionally, the acquired series of diffraction patterns is analysed by sequentially applying the Rietveld method [1] to individual patterns. Often, physical models (for example stress-strain relationships or reaction kinetics) are simply fitted to the output of this analysis. An alternative approach is to incorporate selected physical models into the refinement procedure by expressing refinable parameters as functions of external variables such as time or temperature. This paper describes some of the challenges involved in applying both the traditional sequential and newer parametric analysis techniques to *in situ* data, using a time-resolved neutron diffraction study of $M_{n+1}AX_n$ phase synthesis as an example.

2. Sequential vs Parametric Rietveld Refinement

Traditionally, *in situ* data have been analysed in a sequential manner, with the input conditions for the analysis of an individual data set being taken from the output of the previous data set in the sequence. While this approach is effective in many cases, problems with parameter stability can arise when the concentrations of phases of interest are low, either when they first start to form or towards the end of their decomposition. At these times, the observed intensity is unlikely to be sufficient to support refinement of parameters such as peak profile (as used to estimate crystallite size and strain) and crystal structure (atomic displacement parameters). Some of these stability problems can be overcome by providing limits to parameter values during refinement but selection of these limits is often subjective and based on the experience of the analyst.

An alternative methodology is the so-called parametric refinement approach developed by Stinton and Evans [2] in which constraints on selected values are applied during data analysis. The parametric approach relies on (i) the simultaneous analysis of all data sets in the sequence; and (ii) the constraint of relevant parameters as functions of an external parameter of interest (commonly, applied temperature and/or elapsed time). It is reasonable to assume that, in between major phase changes, some phase related parameters will only vary in a

uniform and predictable manner as functions of the external variable. For example, rather than refining unit cell dimensions for each data set individually, they can be calculated from equations which relate their coefficients of thermal expansion to the measured sample temperature. Using this approach, parameters that may be unstable during sequential refinement are constrained in a way which prohibits their refinement to physically unrealistic values. As fewer independent parameters are required, the parametric approach effectively decreases the parameters-to-observations ratio, thus increasing refinement stability.

It is worth noting that the accuracy and stability of the parametric approach is dependent upon the ability of the selected equations to accurately model the observed changes within the sample [2]. As a result, it is advised that sequential analysis still be undertaken to allow the selection and development of the models used to constrain parameters in this manner.

3. Example - $M_{n+1}AX_n$ Phase Synthesis

Solid-state synthesis of several $M_{n+1}AX_n$ phases is known to involve the formation of short-lived intermediate phases [3]. A time-resolved study of the Ti_3AlC_2 system was conducted on the POLARIS neutron diffractometer [4] at the ISIS neutron facility, to investigate the reaction mechanism. Mixtures of Ti_3C_2 and Al powders in the appropriate stoichiometric ratios to form Ti_3AlC_2 were cold pressed into cylindrical pellets 13mm in diameter by approximately 11mm high. Two such pellets were stacked into a vanadium can which was suspended within a standard ISIS vacuum furnace. In the run described here, the furnace temperature was ramped at 5°C/min from 25°C to 1000°C (data sets 54504 to 54543), held for 220 minutes (data sets 54543 to 54587), then turned off and allowed to cool under its own inertia (data sets 54587 to 54608). Time-of-flight neutron diffraction patterns were collected continuously throughout the heating cycle with 5 minute acquisitions per data set.

Sequential data analysis was undertaken using the TOPAS-Academic [5] software package, with the resultant phase abundances shown in Fig. 1. The graph shows (i) melting of aluminium at data set 54526; (ii) formation and smooth growth of Ti_3AlC_2 between data sets 54544 and 54574; and (iii) the reappearance of aluminium at data set 54574, despite the sample temperature exceeding the melting point of the metal at this stage. This is a result of the aluminium unit cell and crystallite size parameters refining to values which enable the calculated aluminium diffraction pattern to model observed intensity which in reality is due to the other phases or background scattering. Given that the phase abundances are derived using the methodology of Hill and Howard [6] which sums the analysed concentrations to 100wt%, the false presence of aluminium metal in the sample causes the apparent concentrations of Ti_3C_2 and Ti_3AlC_2 to be depressed.

The behaviour of lattice parameters as functions of measured sample temperature for the cubic Ti_3C_2 and aluminium phases is shown in Fig. 2. Notice that the lattice parameter of the Ti_3C_2 phase, which persists throughout the reaction, displays a clear dependence on the temperature of the sample. Initially this is also true of the aluminium lattice parameter; however the dependence rapidly vanishes upon melting.

A parametric analysis was then conducted, with the aim of stabilising the refined parameters and hence improving the determination of phase abundance. Empirical 2nd order polynomial equations for the unit cell dimensions of aluminium and Ti_3AlC_2 (which displays similar erroneous behaviour early in the reaction) as functions of the measured temperature were derived from the relevant, stable portions of the sequential analysis. These equations were coded into a new TOPAS input file, with the coefficients of the equations allowed to refine within suitable limits. The result of analysing all 104 diffraction patterns simultaneously is shown in Fig. 3. The abundance of aluminium metal now correctly reports as 0wt% after melting and the Ti_3AlC_2 phase shows a smooth increase in concentration as the reaction progresses.

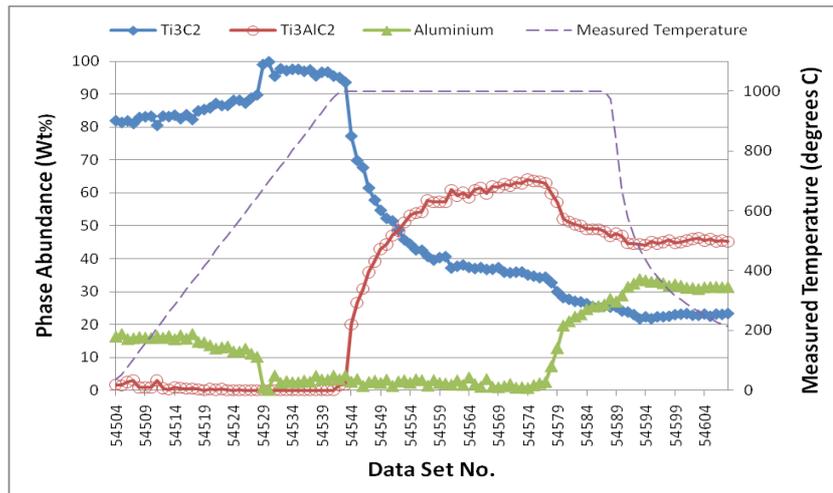


Fig. 1. Phase abundance initially determined by sequential analysis of the *in situ* data. Note the reported formation of aluminium metal beginning at data set 54574 (at 1000°C) and the corresponding decreases in Ti_3C_2 and Ti_3AlC_2 abundances. The temperature profile of the furnace is shown as a dashed line (right axis).

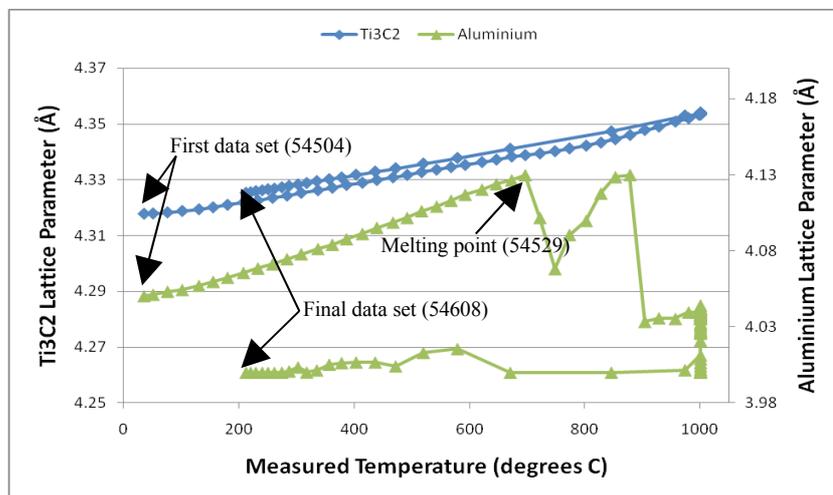


Fig. 2. Lattice parameter values for Ti_3C_2 (left axis) and aluminium (right axis) determined by sequential analysis. The behaviour of the Ti_3C_2 lattice parameter clearly correlates with the temperature of the furnace. However, the aluminium lattice parameter becomes unstable after melting occurs at data set 54526, and refines to values near its lower limit (4.0Å) which was set slightly below its room temperature value.

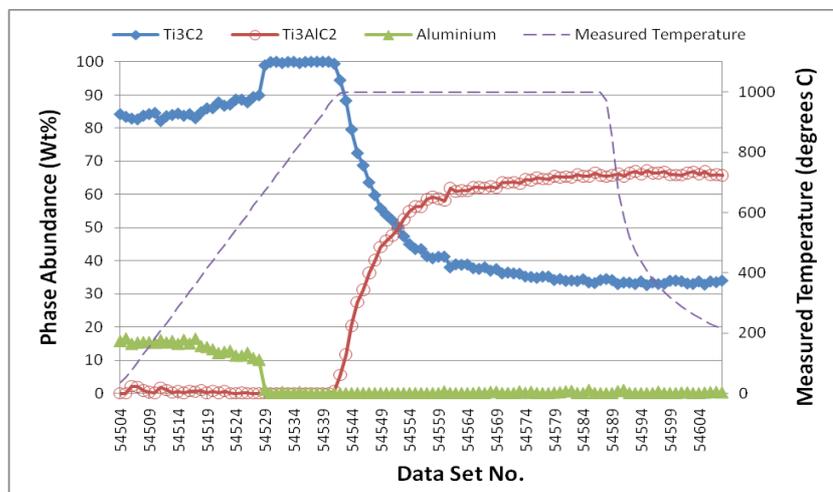


Fig. 3. Phase abundance determined by parametric analysis of the *in situ* data using sample temperature to constrain the lattice parameters of aluminium and Ti_3AlC_2 . Stability of the phase abundance of all three phases has been improved. The temperature profile of the furnace is again shown as a dashed line (right axis).

4. Discussion

During sequential analysis, all parameters are free to refine to values which provide the best fit between observed and calculated patterns. However, in parametric refinement there is the potential for the constraint relationships to compromise this minimisation process. Therefore, confirmation is needed to ensure that the applied models accurately represent the physical and chemical changes occurring in the sample. Fig. 4 shows the weighted profile R-factor (Rwp) for each data set for both the sequential and parametric analysis runs. Under ideal circumstances, these two curves should be identical. While the parametric Rwp values are slightly higher than the equivalent sequential values (indicating either minor errors in the parametric models, or that unrealistically low values of Rwp were achieved in the original sequential analysis) the level of agreement is excellent giving confidence in the models used.

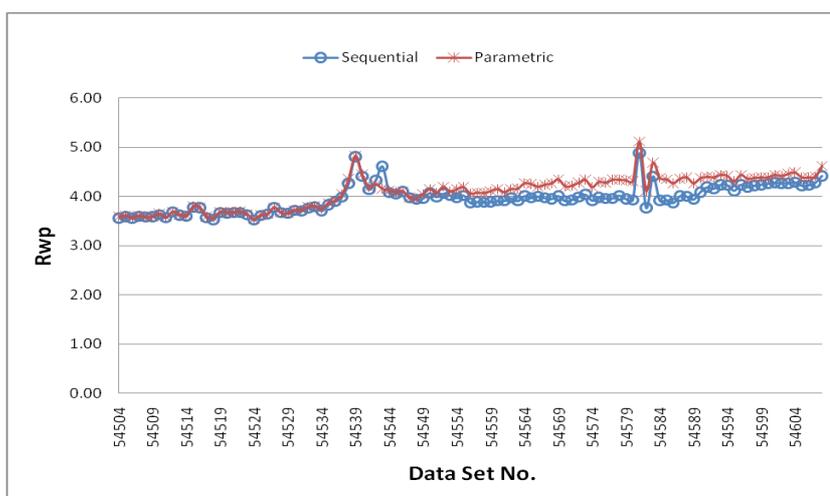


Fig. 4. Comparison of the weighted profile R-factor (Rwp) for both the sequential and parametric approaches. Note the slight deviation after data set 54549, possibly indicating minor errors in the parametric models used.

5. Conclusions

Parametric Rietveld refinement allows physical models to be incorporated into the refinement procedure for the purposes of (i) stabilising refinable parameters; and (ii) evaluating the applicability of the physical models selected to the observed behaviour. This approach reduces the independent parameter-to-observations ratio and enables simultaneous analysis of all data sets in a sequence. However, the parametric approach has the potential to overly constrain parameters and as such, sequential analysis must still be undertaken to allow the selection and development of the models used to constrain parameters.

Acknowledgments

The authors would like to thank Ron Smith from POLARIS at the ISIS pulsed neutron source and Chris Howard for discussions regarding the fitting of time-of-flight data. This work was supported by the Access to Major Research Facilities Program. MJS acknowledges the financial support of AINSE and the CSIRO Light Metals Collaboration Fund.

References

- [1] Rietveld H M 1969 *J. Appl. Cryst.* **2** 65
- [2] Stinton G W and Evans J S O 2007 *J. Appl. Cryst.* **40** 87
- [3] Wu E, Kisi E H, Riley D P and Smith R I 2002 *J. Am. Ceram. Soc.* **85** 3084
- [4] Smith R I, Hull S and Armstrong A R 1994 *Mater. Sci. Forum*, **166–169** 251
- [5] *TOPAS-Academic V4.1* Coelho Software 2007
- [6] Hill R J and Howard C J 1987 *J. Appl. Cryst.* **20** 467