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New horizons for the structural characterization of stainless steel slags by X-ray powder diffraction

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Abstract. The Rietveld method was used to reliably interpret severely superimposed X-ray diffraction patterns of 'reduced AOD slags'. These slags were thermochemically treated in an arc furnace at BAM to recover valuable alloying metals and to convert the residual mineral fraction of the slag into ecologically desirable products. It is shown that recent methodological progress in XRD enables the interpretation of X-ray diffraction patterns of slags by the Rietveld technique, thereby replacing earlier apprehension of the method being generally inapplicable to these materials due to the complexity of the analytical problem.

Introduction

A recent review [1] estimates the annual world production of steel slags to be at least 40 million tons. It also lists some of the economic and ecological necessities continue to demand considerable effort to develop technologies for metal recovery from slags in many countries. AOD (Argon Oxygen Decarburization) slags and EAF (Electric Arc Furnace) slags are by-products of modern stainless steel production processes and contain valuable alloying metals, especially chromium and manganese, in amounts high enough to render metal recovery a profitable business. For a highly-effective metal recovery from 'reduced AOD slags', the thermochemical technology RECARC [2] is currently being developed at BAM. The RECARC project comprises a systematic investigation of the influence of the *operating parameters of an electric arc furnace* and of *chemical additives* on the effectiveness of the metal recovery and on the properties of the thermochemically treated slag. Among other techniques, X-ray powder diffraction (XRD) analyses were carried out for an in-depth analysis of the products. To overcome possible ambiguities in the interpretation of XRD patterns of such demanding multi-phase samples and *to enhance the reliability of the derived analytical results* the Rieveld method (see publications of the IUCr [3] and its Commission on Powder diffraction)

was successfully used. To the best of our knowledge, this method has not yet been applied to stainless steel slags. For a review of previous XRD work on AOD slags see [1].

Samples

The 'as received' materials used for this investigation were two different batches of 'reduced AOD-slag' produced at the same AOD-converter operated at an industrial steel-making facility in Germany. Both slags were the result of a single production cycle. The time span between the two cycles was about two years. Upon receipt at BAM, each slag was homogenized and labelled S1 and S2, respectively. For X-ray fluorescence (XRF), XRD, and some other analytical techniques, a portion of each slag was 'conditioned' by removing – as far as possible - all loose metallic lumps from the remaining oxidic slag component. According to XRF analyses the chemical composition of the 'conditioned' slag S1 is: 39.9 wt% Ca,14.8 wt% Si, 0.5 wt% Al, 1.8 wt% Mg, 2.1 wt% Cr, 1.5 wt% Mn, 0.8 wt% Fe, 0.1 wt% Ti. The CaO/SiO_2 mass ratio is 1.76 ± 0.02. It is assumed that in the 'as received' slags Ca, Si, Al, Mg and Ti occur in their oxidic form only, whereas Cr, Mn and Fe occur both in their metallic as well as oxidic forms. The chemical composition of the conditioned slags S2 is close to that of S1. 20 to 25 kg of *un*conditioned slag were used for each run of the thermochemical treatment, carried out under reducing conditions in the electric arc furnace at BAM. The flexible construction of this furnace allows for the variation of a considerable number of operating parameters, see [2]. The samples this paper reports on are listed in table 1. All samples analysed by XRD were pulverized and homogenized in a vibratory disc mill using a tungsten carbide grinding set.

Table 1 Nomenclature of the samples of slags thermochemically treated at BAM

slag-sample	unconditioned slag used as a starting material	reducing agent	operating parameters of the thermochemical treatment	Rietveld plot
S1a	S1	carbon	*yet to be* optimized	figure 1
S1b	S1	carbon	*partially* optimized	-
S1c	S1	carbon	*largely* optimized	figure 2
S2a	S2	carbon	*largely* optimized	figure 3
S2b	S2	aluminium	*largely* optimized	figure 4

Data collection and data treatment

XRD measurements were performed on a Bruker-AXS D-5000 diffractometer in Bragg-Brentano geometry, using an 1.0 mm aperture slit, a 0.1 mm receiving slit, a sample spinner (0 or 15 rpm), a curved graphite monochromator in the diffracted beam, a scintillation counter and cobalt $K\alpha_{1,2}$ radiation with 40 kV x 30 mA (copper $K\alpha_{1,2}$ radiation with 40 kV x 40 mA for additional measurements on some samples). Data was collected in the 2Θ-range from 5° to 140° in steps of 0.02° using 30 to 50 seconds per step. For the analysis of the diffraction pattern the DiffracPLUS [4] and the BGMN [5] packages were used. All Rietveld analyses of the diffraction patterns of the slag samples employed the fundamental parameter approach [4-6], a low-angle limit (LAL) of 8°, and were assisted by Rietveld

refinements of diffraction patterns of model samples with *simplified* chemical and phase compositions, including synthetic bredigite and various calcium silicates.

Results and discussion

Figure 1 shows a section of the Rietveld plot of sample S1a, which was thermochemically treated under *yet to be* optimized operating conditions. As a consequence, large portions of the chromium oxide and manganese oxide components of this slag were not reduced to the corresponding metals, but recrystallized as a $(Mg,Mn)Cr_2O_4$ spinel phase (see table 2).

Table 2. Results of qualitative and semi-quantitative phase analyses of five samples of thermochemically treated 'reduced AOD slags'; data from Rietveld analyses with LAL = 8° and HAL = 100°. For agreement indices see the inset in the upper right corners of figures 1-4, which are representative for sample S1b as well.

slag sample number	weight fraction / %								
	1.	2.	3.	4.	5.	7.	8.	9.	10.
	β-C_2S	γ-C_2S	bredigite	melilite	merwinite	Cr-spinel	perovskite	vaterite	calcite
S1a	31	7	54	-	3	4	-	1	-
S1b	27	46	17	5	1	-	-	3	1
S1c	68	4	12	7	4	-	-	2	2
S2a	85	4	11	-	-	-	-	-	-
S2b	74	6	2	17	-	-	1	-	-

Figure 2 shows a section of the Rietveld plot of sample S1c, which was thermochemically treated under *largely* optimized operating conditions, leading to the reduction of the chromium and manganese oxides to a metal phase which separated from the molten slag due to the large difference in density. The diffraction pattern and its evaluation by the Rietveld method reveal not only the complete absence of the $(Mg,Mn)Cr_2O_4$ spinel phase from the samples S1b and S1c, but also the existence of considerable differences in the mass fractions of the other mineralogical phases in the three thermochemically treated samples S1a, S1b and S1c, all derived from the same initial slag S1.

Figure 3 shows a section of the Rietveld plot of sample S2a, which was thermochemically treated under *largely* optimized operating conditions. This diffraction pattern and the results of phase quantification by the Rietveld method show that the phase composition of the samples S1c and S2a is not identical, although both were treated under largely optimized operating conditions. These differences are interpreted as consequences of minor differences in the chemical composition of the two initial slags S1 and S2.

Figure 4 shows a section of the Rietveld plot of sample S2b, thermochemically treated under *largely optimized* operating conditions, but using gritty metallic aluminium instead of coke for reducing agent. The comparison of figures 3 and 4 and of the corresponding data in table 2 reveals considerable differences in the mineralogical composition of slag samples S2a and

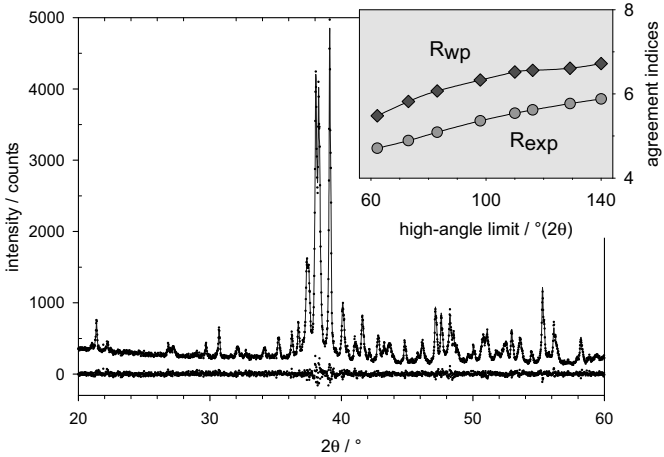

Figure 1. Observed (dotted line) and calculated (solid line) diffraction pattern, difference curve and agreement indices (small box) for the Rietveld analysis of the diffraction pattern of sample S1a

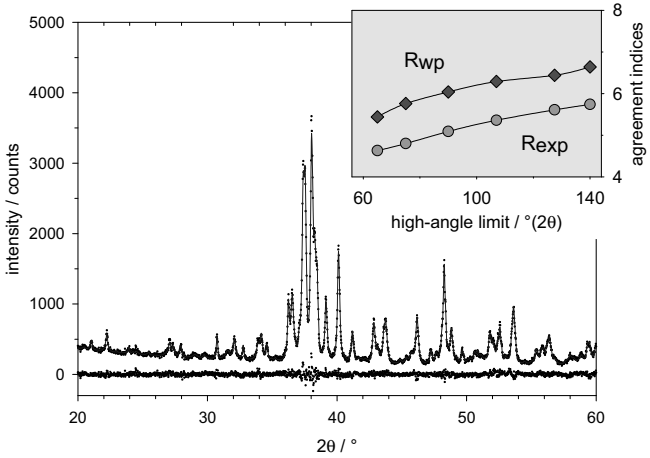

Figure 2. Observed (dotted line) and calculated (solid line) diffraction pattern, difference curve and agreement indices (small box) for the Rietveld analysis of the diffraction pattern of sample S1c

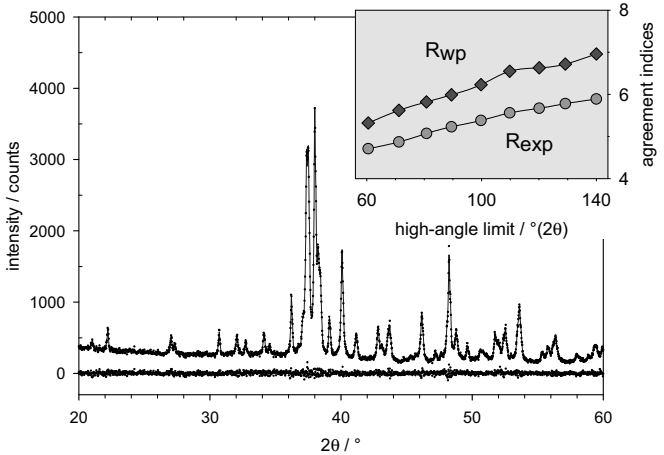

Figure 3. Observed (dotted line) and calculated (solid line) diffraction pattern, difference curve and agreement indices (small box) for the Rietveld analysis of the diffraction pattern of sample S2a

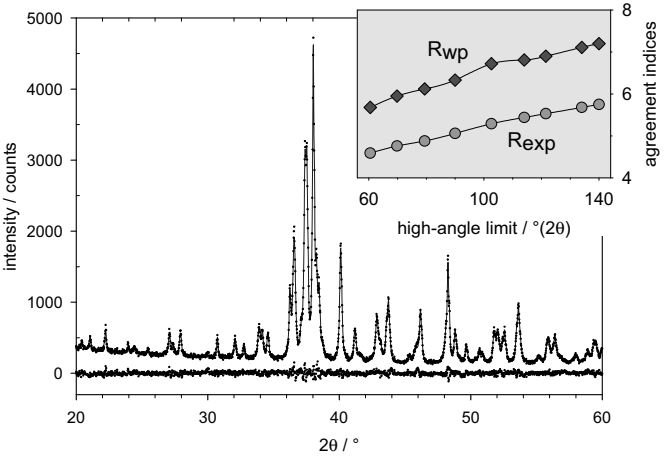

Figure 4. Observed (dotted line) and calculated (solid line) diffraction pattern, difference curve and agreement indices (small box) for the Rietveld analysis of the diffraction pattern of sample S2b

S2b, although both are derived from the same initial slag S2. The most striking feature of sample S2b is the exceptional high mass fraction of melilite, a mineralogical phase that can be interpreted as a solid solution of gehlenite and akermanite, accompanied by a substantial reduction of the mass fraction of bredigite due to the competition of these two mineralogical phases for the very limited amount of MgO in slag S2.

The exceptional high quality of the data evaluation of the diffraction patterns of these slags achieved by the Rietveld method is documented by the Rietveld plots shown in figures 1-4, as well as by the very good agreement indices. The small insets in the upper right corners of figures 1-4 result from repeated Rietveld refinements carried out on the same diffraction pattern systematically varying the high-angle limit (HAL). The results of (semi)-quantitative phase analyses (QPA) summarized in table 2 are also stable against variations of the HAL. The XRD results are in accordance with the results of complementary analytical techniques, such as X-ray Fluorescence Analysis, Scanning Electron Microscopy and Thermogravimetry.

Concluding remarks

XRD is an established, powerful analytical technique for the structural characterization of slags, although the interpretation of the diffraction patterns of slags is not always unambiguous. The present XRD investigation of thermochemically treated 'reduced AOD slags' has shown that the Rietveld method, which – to the best of our knowledge – has not yet been applied to stainless steel slags, provides unique opportunities for the validation of the results of *phase identification* and – for the first time – makes possible *(semi)quantitative phase analyses* of slags. Earlier apprehension in the slag research community, as to whether the complexity of the analytical problem generally excludes the application of whole-powder pattern techniques to the interpretation of diffraction patterns of slags, is therefore superseded by the achieved methodological progress. The outcome of this investigation serves as a basis for a better understanding of the phase formation processes associated with the economically and ecologically desirable metal recovery from stainless steel slags.

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