Why Can GDS Analyze Grey Iron and Other As-Cast Materials?

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Instrument: GDS

Glow discharge spectrometry (GDS) is capable of analyzing all types of cast irons while other techniques, especially spark-emission spectrometry, commonly struggle in this area. This capability arises from several features of glow discharge sputtering that decidedly differentiate these techniques. For GDS, a wet 600-grit finish is recommended. This limits the extent to which carbon flakes are removed from the surface. When phases are not elementally distinct, as in white iron, there is virtually no difference in sputtering rate across the sample, leading quickly to steady, representative signal. During the analysis of as-cast samples, including grey and ductile irons, a longer pre-burn period is needed. With multi-phase samples, different phases (in this case, ferrous material and graphite) can sputter at different rates, resulting in a changing signal for each phase as the slower sputtering graphite is relatively enriched on the surface. Ultimately, an equilibrium is reached, in which the surface concentration is constant for each element. Slower sputtering elements continue to sputter more slowly, however, surface enrichment of these phases is proportional to their sputtering rate, leading to an accurate result.

To help illustrate the need for a longer pre-burn, cast iron samples were analyzed with a LECO GDS850A. The resulting compositional depth profile (CDP) data shows the relation of the carbon, silicon, iron and sulfur signals to both time and depth. As shown in Figure 1, signal does not stabilize for C and Si for nearly 300 s after sputtering begins (A). Accordingly, such time is necessary before calculated composition is accurate. Although the depth axis is a good approximation of the analysis depth, these data should not be interpreted to indicate that carbon concentration increases as a function of depth from the surface in the sample itself; apparent surface composition of carbon is enriched during analysis due to a slower sputtering rate to a level that yields an accurate result (B).

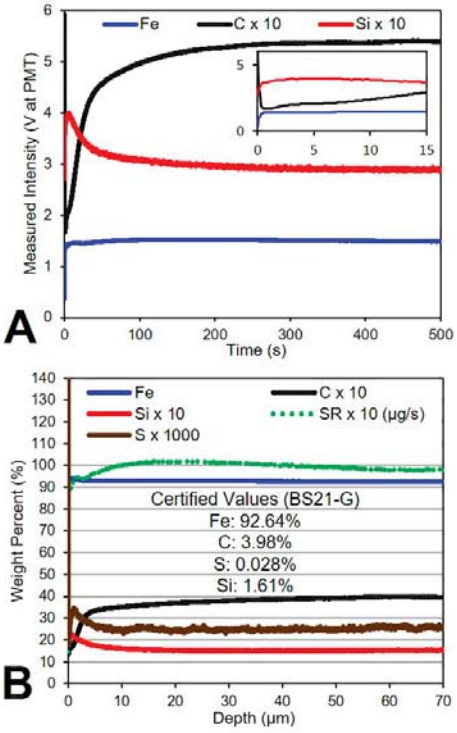

Figure 1: Depth profiling grey cast iron standard. A) Stabilization of signal is apparent after approximately 300 s of sputtering, with rapid change occurring in the first 15 s (inset). B) Stabilization of concentration at certified concentration values as analysis progresses. In addition to signal, calculated sputtering rate (SR) also stabilizes. Note, traces for C, Si, and SR are multiplied by 10 for scaling. Bulk analysis data can be found on the next page.

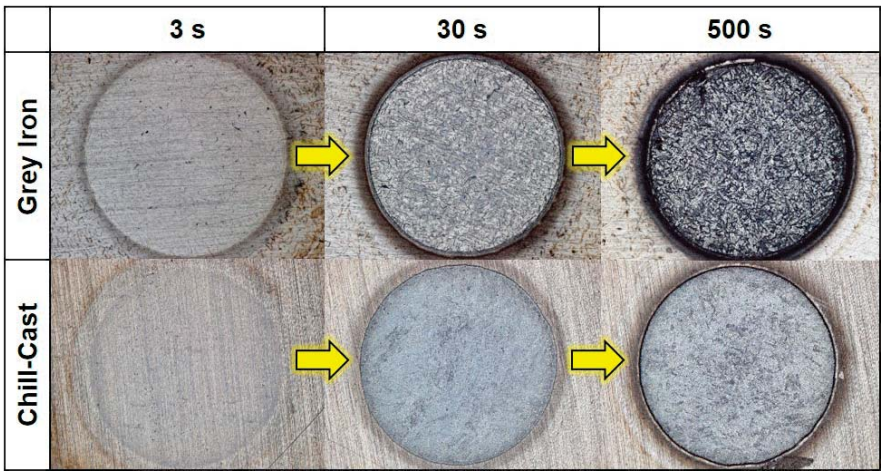

Figure 2: Differences in physical changes on the surface of grey iron (top) and white iron (bottom) during glow discharge sputtering. Changes to white iron are mostly complete in the first 30 s, while grey iron continues to have increased concentrations of carbon on its surface.

Spectroscopy Performance Note

Spectroscopy Performance Note

During the sputtering process, the surface undergoes a dramatic visual transformation. As shown in Figure 2, graphitic carbon increases dramatically in grey iron as sputtering proceeds, with major changes after 30 s of sputtering. Conversely, most major changes for chill-cast white iron are complete after just 30 s. In the case of chill-cast white iron, carbon is not present within iron-rich austenite and cementite phases and sputters at a rate consistent with the surrounding materials.

Data from these experiments are similar to those conducted by LECO's Zdenek Weiss and published in Spectrochimica Acta, Part B[1].

What Happens in Spark OES?

In the high-energy pre-spark, the surface of the sample is melted into a surface ready for analysis. This is frequently referred to as homogenization, but visual observation points to a remarkably non-homogeneous melt spot due to heat dissipation from the center to the edges, and related movement of elements and various phases in the sample. Figure 3 emphasizes two decidedly different regions of a spark spot that can be further contrasted with the portion of the sample outside the spot. Outside the spot, graphitic flakes can be observed as distributed throughout the surface. Fewer flakes exist as you move from the outer white circle inward to the yellow circle. Inside the yellow circle, there is no semblance of the outer graphite flakes. The dark spots that resemble graphite nodules are actually depressions due to ablation in the spark discharge. The general depletion of carbon in the center of the melt spot is believed to be due to sublimation of portions of the graphite when grain boundaries are preferentially attacked as anchor points for the spark discharge. In contract, with GDS, the physical process of sputtering continuously reveals and samples virgin material, meaning there is no appreciable induced mixing of layers, and the crater has a homogeneous distribution of sample constituents.

Figure 3: Developed heterogeneity in a spark discharge melt spot. Differences in the surface are clearly discerned between each region of the melt spot and the surrounding material.

Confirmation of the Capability of GDS to Determine for Carbon in As-Cast Materials

With an understanding of how the differences in GDS and Spark-OES physically manifest, the question then becomes how accurately is carbon determined in as-cast. Table 1 shows good agreement between a certified reference material for as-cast grey iron and the results generated with a GDS-500. These data are related directly to the calibration curves for the selected as-cast method without additional data processing. Additional data are available for other types of cast iron in the GDS Performance Note Library (Analysis of Cast Irons, 209-076-026).

Table 1: Experimental GDS results for the bulk analysis of BS21A-G, a certified reference material for grey iron.

ELEMENT	AVERAGE	CERT	STDEV	RSD
C	3.87	3.83	0.023	0.60
Cr	0.10	0.10	0.0003	0.33
Cu	0.23	0.23	0.0004	0.16
Mn	1.18	1.18	0.003	0.27
Mo	0.19	0.19	0.001	0.35
Ni	0.20	0.19	0.001	0.34
P	0.076	0.07	0.001	1.85
S	0.016	0.018	0.001	6.72
Si	1.56	1.56	0.016	1.02
V	0.016	0.016	0.001	3.57
Ti	0.015	0.014	0.0003	1.63
Al	0.021	0.02	0.0001	0.27
Fe	92.53	92.64	-	-

[1]*Zdenek Weiss. Spectrochimica Acta, Part B: Atomic Spectroscopy. 51(8):863-876, July 1996.*

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