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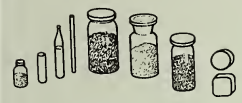

Standard Reference Materials:

HOMOGENEITY CHARACTERIZATION OF NBS SPECTROMETRIC STANDARDS III: WHITE CAST IRON AND STAINLESS STEEL POWDER COMPACT

U.S. Department of Commerce
National Bureau of Standards

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Standard Reference Materials:

Homogeneity Characterization of NBS Spectrometric Standards III: White Cast Iron and Stainless Steel Powder Compact

H. Yakowitz, D. L. Vieth, and R. E. Michaelis

Institute for Materials Research
National Bureau of Standards
Washington, D.C.

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PREFACE

Within the framework of the NBS Institute for Materials Research the area of standard reference materials is a broad and important one, including the preparation, characterization and distribution of a wide variety of materials in such diverse fields as metallurgy, polymers and inorganic materials. In carrying out such a program there is much interaction with representatives of industry and science, beginning with discussions as to which primary standard materials will do most to advance technology, the furnishing of materials and fabrication of samples, and the characterization and certification of the materials by cooperative efforts. The many groups participating in a standards program are very interested in detailed information on specific aspects of the program -- but to date there has been no publication outlet for such written discussions.

To meet this need, NBS Miscellaneous Publication 260 has been reserved for a series of papers in the general area of "standard reference materials". This series will present the results of studies and investigations undertaken within the Institute for Materials Research with emphasis on the preparation and characterization of standard reference materials. This subject-oriented series will provide a means for rapid dissemination of this detailed information and we hope will stimulate the use of standard reference materials in science and industry.

W. Wayne Meinke, Chief
Office of Standard Reference Materials

OTHER NBS PUBLICATIONS IN THIS SERIES

NBS Misc. Publ. 260, Standard Reference Materials: Catalog and Price List of Standard Materials Issued by the National Bureau of Standards, October 1965. 45 cents.* (Supersedes NBS Misc. Publ. 241, March 1962.)

NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, June 1964. 30 cents.*

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CONTENTS

STANDARD REFERENCE MATERIALS: HOMOGENEITY CHARACTERIZATION OF NBS SPECTROMETRIC STANDARDS III: WHITE CAST IRON AND STAINLESS STEEL POWDER COMPACT

H. Yakowitz, D. L. Vieth, R. E. Michaelis

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ABSTRACT

This paper describes a continuation of the NBS effort to characterize metal materials as to their suitability for use in calibrating microanalytical techniques such as the solids mass spectrometer and, especially, the electron probe microanalyzer. An NBS white cast iron sample (SRM 1175) and a specially prepared stainless steel powder metallurgy compact have been investigated by means of electron probe microanalysis and optical metallography. Results for six elements in the cast iron and three in the stainless steel are given. It is concluded that neither of these materials is suitable for use for calibration in microanalytical techniques. It is emphasized, however, that this in no way affects the usefulness of the white cast iron material for macroanalytical techniques such as optical emission and x-ray spectrochemical analysis.

Key words: microanalytical techniques, solids mass spectrometer, electron probe microanalyzer, NBS white cast iron sample (SRM 1175), stainless steel powder metallurgy compact, optical metallography, macroanalytical techniques, optical emission, x-ray spectrochemical analysis

PART I: WHITE CAST IRON

In the continuing program to characterize existing NBS Standard Reference Materials as to their suitability for microanalytical techniques such as for the electron probe microanalyzer and the solids mass spectrometer, the white cast iron designated SRM 1175 [1] was investigated. The certified composition values for this material are given in table I [2].

It was decided to investigate the homogeneity of several elements by taking mechanical line scans with the electron probe microanalyzer in precisely the same manner as was done on NBS-SRM standards for brass and for low-alloy steel [3]. A portion of the chill-cast face was prepared metallographically by grinding on SiC papers through 600 grit and polishing to a final finish on 6- and 0.25-micron diamond respectively. No pits or inclusions were observed; as expected, etching revealed no smeared metal. The resultant structure is shown in figure 1. After removing the etch on 0.25 micron diamond, the sample was introduced into the electron probe microanalyzer.

Mechanical line scans were taken for six of the eighteen certified elements: namely, Mn, Si, Ni, Cr, Mo and Fe. Portions of each of these traces are shown in figure 2; the total sample length examined for each element ranged from 1.2 to 2.0 mm. The traces show that the elements investigated are not homogeneously distributed at micron levels of spatial resolution. Therefore, SRM white cast iron 1175 is not considered suitable for microanalytical techniques in that reproducible results do not appear possible.

It is emphasized, however, that this in no way affects the usefulness of Standard Reference Material 1175 for macroanalytical techniques such as optical emission and

x-ray spectrochemical analysis in which a large portion of the chill-cast face is sampled. Further detailed information on the macrohomogeneity of this material may be obtained from reference [1].

REFERENCES

[1] R. E. Michaelis and L. L. Wyman, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, NBS Misc. Publ. 260-1, 31 pp, (1964).

[2] J. I. Shultz, Standard Reference Materials: Methods for the Chemical Analysis of White Cast Iron Standards, NBS Misc. Publ. 260-6, 62 pp, (1965).

[3] H. Yakowitz, D. L. Vieth, K.F.J. Heinrich, and R. E. Michaelis, Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards II: Cartridge Brass and Low-Alloy Steel, NBS Misc. Publ. 260-10, 28 pp, (1965).

Table 1. Certified composition values for SRM 1175, white cast iron (Fe by difference is 87.22%).

	Average (%)		Average (%)
Carbon	1.97	Molybdenum	1.51
Magnesium	1.64	Cobalt	0.11
Phosphorus	0.652	Tin	0.025
Sulfur	0.017	Titanium	0.35
Silicon	3.48	Arsenic	0.22
Copper	1.50	Boron	0.00_5
Nickel	2.98	Antimony	0.020
Chromium	2.43	Tellurium	0.009
Vanadium	0.221	Lead	0.003

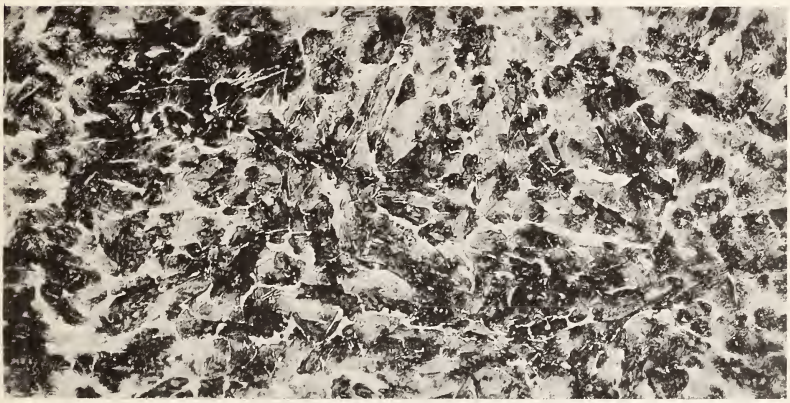


Figure 1. NBS-SRM 1175, white cast iron. (X500).

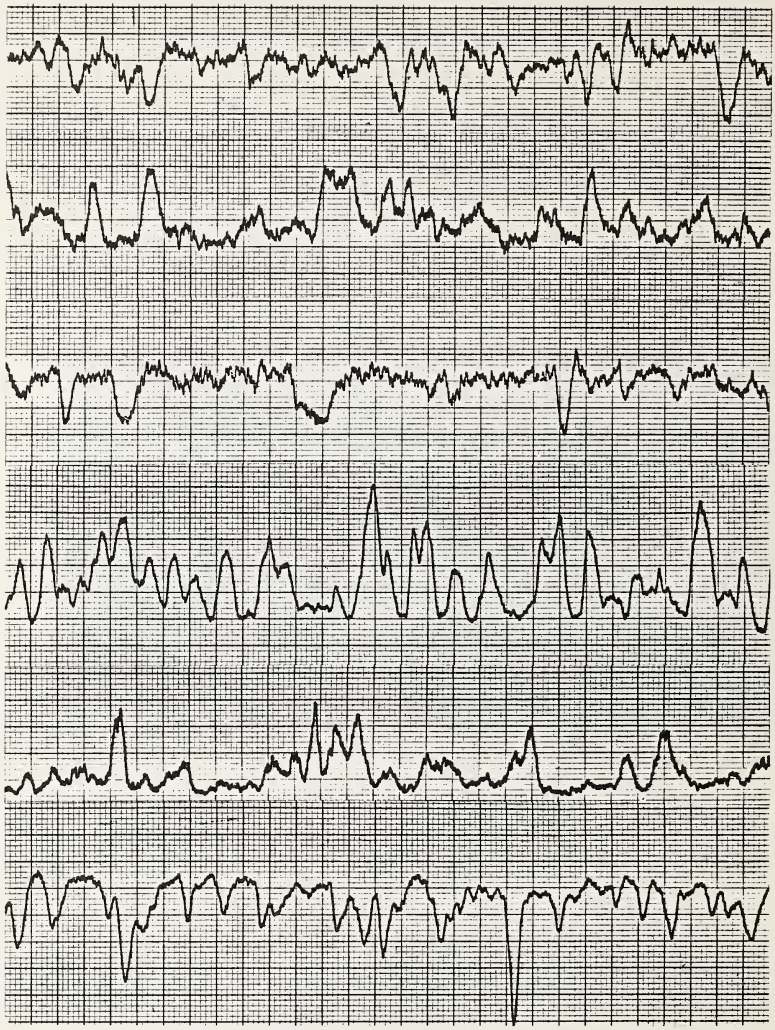


Figure 2. Ratemeter recordings for six elements in NBS-SRM 1175, white cast iron. All specimens were driven at 96 microns per minute with respect to the stationary electron beam. Chart represents 600 microns in length.

PART II: STAINLESS STEEL POWDER COMPACT

1. INTRODUCTION

As part of the NBS Program to prepare and provide standard reference materials of suitable homogeneity that any micro- or macro-analytical technique can be carried out without fear of inaccuracy due to inhomogeneity, it was decided to obtain an 18Ni-Cr8 stainless steel of precise composition. It was the considered opinion of the NBS scientists responsible that this stainless steel best could be prepared by means of powder metallurgical techniques. Specifically, it was felt that weighing Fe, Ni and Cr powders of the finest size available to within 0.001% of the desired values, followed by pressing and sintering to yield a billet, was necessary; this billet would then be worked and annealed to further improve homogenization.

Due to the lack of direct NBS facilities to carry out such a program, it was necessary to arrange for this work on a contract basis. The Powder Process Laboratory of the General Electric Research and Development Center undertook to prepare the desired material. Scientists in this laboratory expressed apprehension at the NBS approach but only because of the difficulties encountered in obtaining fine (less than 10 micron), pure, oxygen-free metal powders - especially chromium. What follows describes the G. E. procedure for preparing the material which was supplied to NBS.

2. MATERIALS

Powders were obtained on a "best available" basis. The limited supply of iron powder dictated the size of the billet made. Chromium was supplied as the finest size available with minimum contamination. The analysis quoted by the supplier was as follows:

Oxygen	300 ppm
Nitrogen	20
Hydrogen	2
Carbon	150
Sulfur	40
Iron	900
Nickel	400
Calcium	800
Chromium	99.74% (by difference)

The powder was approximately 80 micron particle size, so that it was necessary to mill for 36 hours in toluene in a nickel ball mill to attain a size comparable with the iron and nickel used (viz., 10 microns or less).

The iron and nickel powders were quoted as being 99.99% pure, but no further analysis was supplied. Microscope observation showed the powder to be in the low micron range, about 10μ or less.

3. PREPARATION

3.1 Weighing and Blending

The three powders were weighed out at the Advanced Technology Laboratories of the General Electric Company. Mixing was effected by rolling the powders for three hours in one-gallon glass jar. The mixture was then packed into a rubber balloon and isostatically pressed at 30,000 psi. A powder billet approximately 2-1/2" diameter x 3" long was obtained.

3.2 Heat Treatment

The green billet was sintered in pure dry hydrogen (-80 °C dew point) followed by a soak at 1200 °C for four hours. The sintered metal was cooled in the furnace. Test strips of clean stainless steel put in alongside the samples came out of the furnace clean and shiny. A metallographic sample taken at this time showed that the product was not homogeneous. Areas believed to be agglormerated chromium

were observed. These particles, however, were approximately twice as large as the particle size of the ingoing chromium powder.

3.3 Mechanical Working and Heat Treatment

In order to promote homogenization the billet was hot extruded. To do this the billet was machined dry into a right cylinder and fitted into a low-carbon steel can. Machining was done under especially clean conditions. The extrusion can was sealed by electron beam welding after pumping down overnight. The canned billet was then heated in dry hydrogen to 1075°C in 2.5 hours, and extruded from 2-1/8" diameter down to 5/8" diameter (11.6/1 area reduction).

The extruded product was annealed for 8 hours at 1300°C in dry hydrogen. This, however, failed to homogenize the sample as shown by metallographic examination. Similarly, further annealing at 1350°C for 15 hours failed to bring about the desired structure. The annealed extrusion was swaged to 0.275" at 850-950°C. A small piece was further swaged at room temperature from 0.275" down to 0.249". Both samples were annealed in pure dry hydrogen for (1) 72 hours at 1350°C and (2) 168 hours at 1400°C.

4. DISCUSSION

Metallographic examination at the various stages of the processing has revealed that working and annealing failed to break up the chromium aggregates. The reason for the formation of these hard particles was not clear, especially since they were larger than the powders used in processing. It was noted that these materials appear to be closely associated with an oxide constituent also observed in the matrix. This is particularly evident in the 750X micrograph of the material in the extruded and

swaged condition where it can be seen that, even though these particles had been severely deformed, an enveloping oxide film was still present (figure 1). The contamination is believed to be inherent in the commercial starting materials, since the test strips of clean stainless steel fired in the same furnace remained bright. It is suggested that although the overall furnace atmosphere was reducing to chromium, the oxide intimately associated with the chromium was not reduced because the powder billet densified readily leaving such areas cut off from dry hydrogen.

Samples of this stainless steel sent to NBS for metallographic examination confirmed the G.E. observations (figure 1). Nevertheless, it was decided to subject the specimens to electron probe microanalysis. Figure 2 shows scanning images for Fe, Cr and Ni. It is apparent that none of these three elements are homogeneously distributed. Oxygen was not studied since the O-K line lies between the Cr-Lα and Cr-L_1 lines and cannot be separated from either. Random point counts (avoiding Cr-rich areas insofar as possible) listed in table 1 show swings of as much as 20% of the Ni and Fe in ferrite depending on position.

Therefore, it must be concluded that this attempt to produce stainless steel of high homogeneity by powder metallurgical techniques has failed. However, signal success has been achieved in preparing homogeneous W-20% Mo by a similar powder process thus indicating the usefulness of this approach. It seems clear that the failure of the stainless steel preparation rests solely on the impossibility of obtaining suitable Cr starting powder.

5. REFERENCE

[1] P. Duncumb and D. A. Melford, Quantitative Applications of Ultra-soft X-ray Microanalysis in Metallurgical Problems, Tube Investments Res. Lab. Tech. Rept. No. 195, 27 pp (1965).

Table 1. Twenty second count totals of points in ferrite for Fe and Ni in stainless steel powder compact. Kα line of Fe and Ni monitored with a LiF crystal at 25 kV.

Point	Ni	Fe
1	61,406	526,653
2	54,940	520,080
3	48,840	405,734
4	53,178	459,058
5	43,334	552,068
6	72,332	517,474
7	50,706	544,124
8	56,592	488,173
9	61,882	535,193
10	54,840	537,676
11	57,860	513,749
12	58,282	527,730
In Cr rich area	4,230	13,314

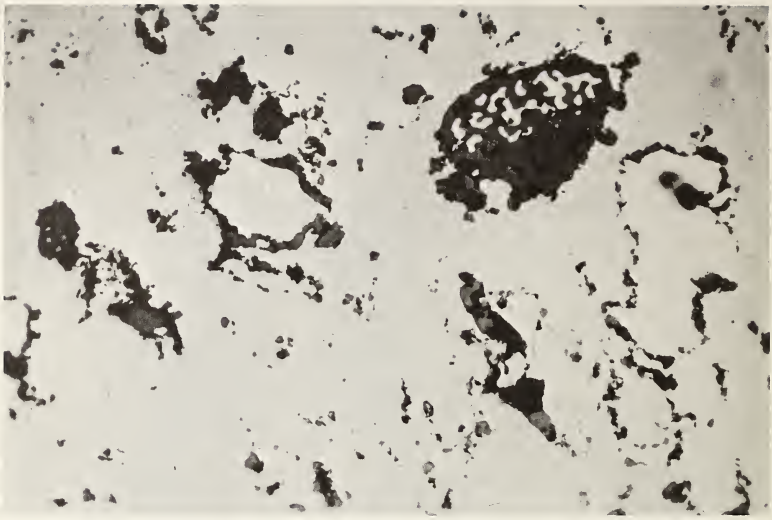
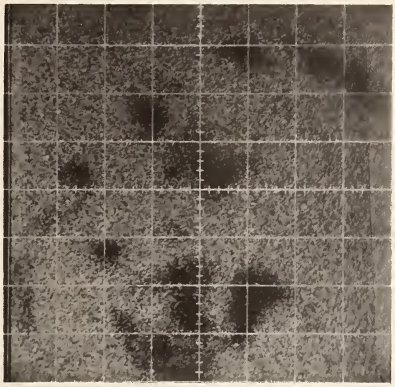


Figure 1. Final submitted stainless steel powder compact. Unetched X750.



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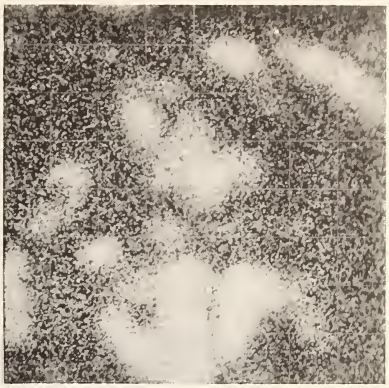

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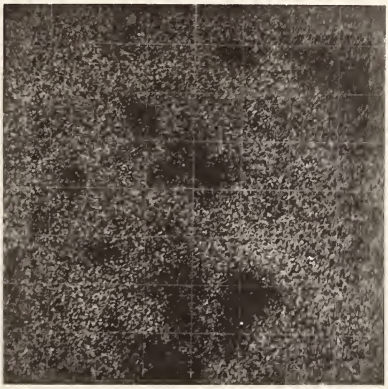

2c

Figure 2. X-ray scanning displays for Fe, Cr and Ni at 500X. 2a. Fe-Kα at 25 kV. 2b. Cr-Kα at 25 kV. 2c. Ni-Kα at 25 kV.

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