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NBS SPECIAL PUBLICATION 260-25

Standard Reference Materials:

**A STANDARD REFERENCE MATERIAL
CONTAINING NOMINALLY FOUR PERCENT
AUSTENITE**

**U.S.
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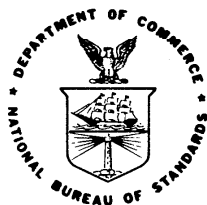
UNITED STATES DEPARTMENT OF COMMERCE • Maurice H. Stans, *Secretary*
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, *Director*

Standard Reference Materials:

**A Standard Reference Material Containing
Nominally Four Percent Austenite**

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Washington, D.C. 20234**



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TABLE OF CONTENTS

	PAGE
Introduction	2
General Description of the Standard	2
Preparation of the Compacts	3
Characterization of SRM-485	8
Conclusions	13
Acknowledgements	14
References	14

LIST OF TABLES

<u>Table No.</u>	PAGE
1. Chemical Analysis of Starting Powder Particles - Content in Weight Percent	3
2. Determinations for Establishing X-ray Calibration Curve of Figure 6	10
3. Comparison of QTM and X-ray Fluorescence Results	12

LIST OF FIGURES

<u>Figure No.</u>	PAGE
1. Scanning electron micrographs of the starting powders	4
2. Fabrication steps for SRM-485	5
3. Structure of finished compacts - etched . . .	6

4.	Cross-section of typical compact	7
5.	Strip-chart recording of Ni-K α signal vs. position in microprobe trace: a = Ni-signal in austenite particle, b = Ni-signal in ferritic matrix, c = Ni-signal at austenite- ferrite matrix. Full scale about 10,000 counts/second	9
6.	Calibration curve for X-ray fluorescence analysis characterization of SRM-485	11
7.	Number of samples in each composition range from 3.0 to 5.3 percent austenite. The total population of 134 standard samples is repre- sented	13

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This standard was produced by powder metallurgical techniques using known amounts of austenite. Using these techniques, 134 specimens were prepared. Because these standards are expected to be used primarily for the calibration of X-ray diffraction equipment, only one surface of each standard is certified, and these surfaces range from 3.1 percent to 5.2 percent in austenite content. To make the specimens, 310 stainless steel powder (austenitic) was blended with 430 stainless steel powder (ferritic) to make a mixture of 5 percent austenite in ferrite. The material was compacted, sintered, polished and etched so the austenite appears white and the ferrite, a deep brown. Then quantitative microscopy methods were used to determine the percentage of austenite near the surface. Furthermore, the 310 powder contains 20 percent of nickel while the 430 powder contains virtually no nickel. Therefore, after establishing a meaningful calibration curve, X-ray fluorescence analysis for the nickel content was also used as a direct measurement of the amount of austenite on the surface of the compact. Both procedures were carried out on fifteen specimens statistically selected from the total number of compacts produced. Agreement, within experimental error limits, was obtained between the X-ray fluorescence results and quantitative microscopy results. The X-ray fluorescence method was used to characterize all additional compacts. X-ray diffraction determinations of austenite content are in good agreement with the X-ray fluorescence and quantitative microscopy results. The compacts may be used as X-ray diffraction standards for austenite or in special cases as X-ray fluorescence standards for nickel content.

Key words: Austenite in ferrite; electron microprobe;
powder metallurgy; quantitative microscopy;
SRM: X-ray fluorescence analysis.

INTRODUCTION

Standard reference materials for retained austenite determination are required because the amount of retained austenite in ferrous material critically affects metallurgical properties. The percentage of retained austenite in ferrous materials is usually determined by X-ray diffraction procedures requiring an accurate measurement of the integrated intensity under two or three selected diffraction peaks. As the amount of retained austenite decreases, however, the accuracy of the intensity measurement deteriorates. Therefore, the National Bureau of Standards has undertaken to produce a series of standards containing from 1 to 25 percent austenite. The first of these standards is now ready for issue. This standard was prepared by means of powder metallurgical methods.

The purpose of this report is to give a detailed description of the preparation and characterization of the present group of 134 specimens. Because completely homogeneous blending of the austenite and ferrite powders used to make the compacts can not be achieved, despite considerable effort, each of the 134 specimens has been separately characterized for austenite content.

GENERAL DESCRIPTION OF THE STANDARD

This standard was prepared by mixing 5 percent by weight of fully austenitic stainless steel powder (type 310) with ferritic stainless steel powder (type 430). Large amounts of chromium and nickel are contained in the 310 stainless steel. Hence, the diffusion of a portion of these elements into the 430 stainless steel would not be expected to alter the austenite structure of the 310 stainless steel. The compact is 20.6 mm (13/16 in.) diameter by 2.54 mm (0.100 in.) thick. One surface is polished and etched so that the austenite is white and the ferrite is a deep brown.

It is this surface which has been characterized with respect to austenite content.

The standard is issued with one surface certified for austenite content. No surface preparation is necessary. In fact, damage to the certified face renders the sample useless. The lowest actual amount of austenite in the certified faces of the samples is 3.1 percent, and the highest value is 5.2 percent.

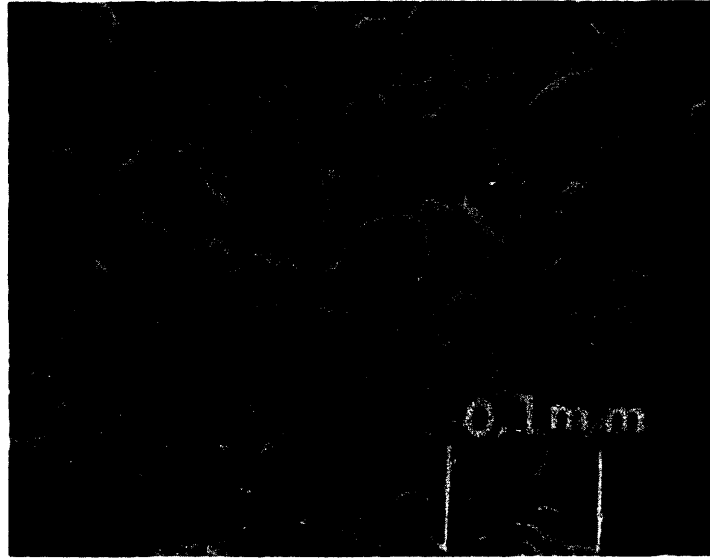
PREPARATION OF THE COMPACTS

The starting powders were irregularly shaped but uniformly sized. The entire lot of 310 powder passed through a 53 μ m sieve but none passed through a 44 μ m sieve. All the 430 powder passed a 44 μ m sieve but none passed a 37 μ m sieve. Figure 1 shows the starting powder particles in detail. The chemical analysis of the powders is shown in table 1.

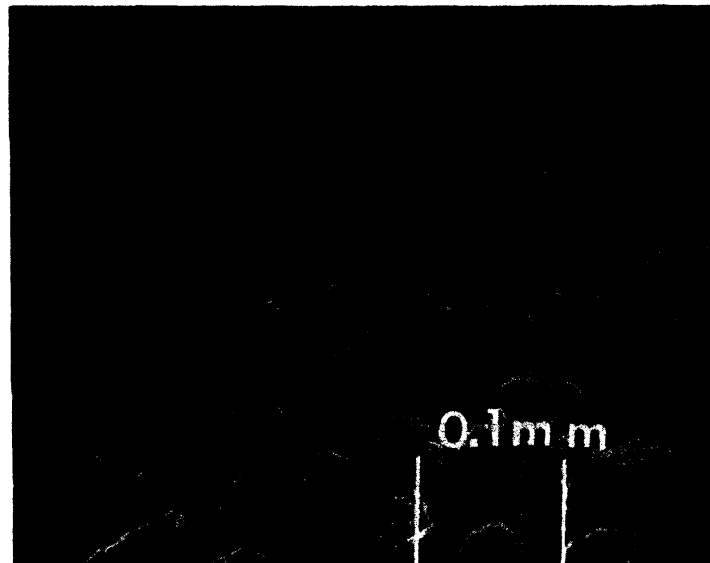
Table 1. Chemical Analysis of Starting Powder Particles - Content in Weight Percent.

<u>Elements</u>	<u>310 Stainless Steel</u>	<u>430 Stainless Steel</u>
Chromium	24.99	16.03
Nickel	20.41	0.09
Iron	53.5	83.5
Carbon	0.05	0.05
Manganese	0.20	0.10
Phosphorus	0.01	0.011
Sulfur	0.007	0.01
Silicon	0.75	0.40

Each step in the preparation of the compacts is shown in the flow diagram given in figure 2. The structure of the final compact was examined by optical and scanning electron microscopy. Figure 3 shows typical microstructural details. The compacts contain several percent porosity and



a



b

Figure 1. Scanning electron micrographs of the starting powders.
a. As received 310 stainless steel powder-fully austenitic.
b. As received 430 stainless steel powder-ferritic.

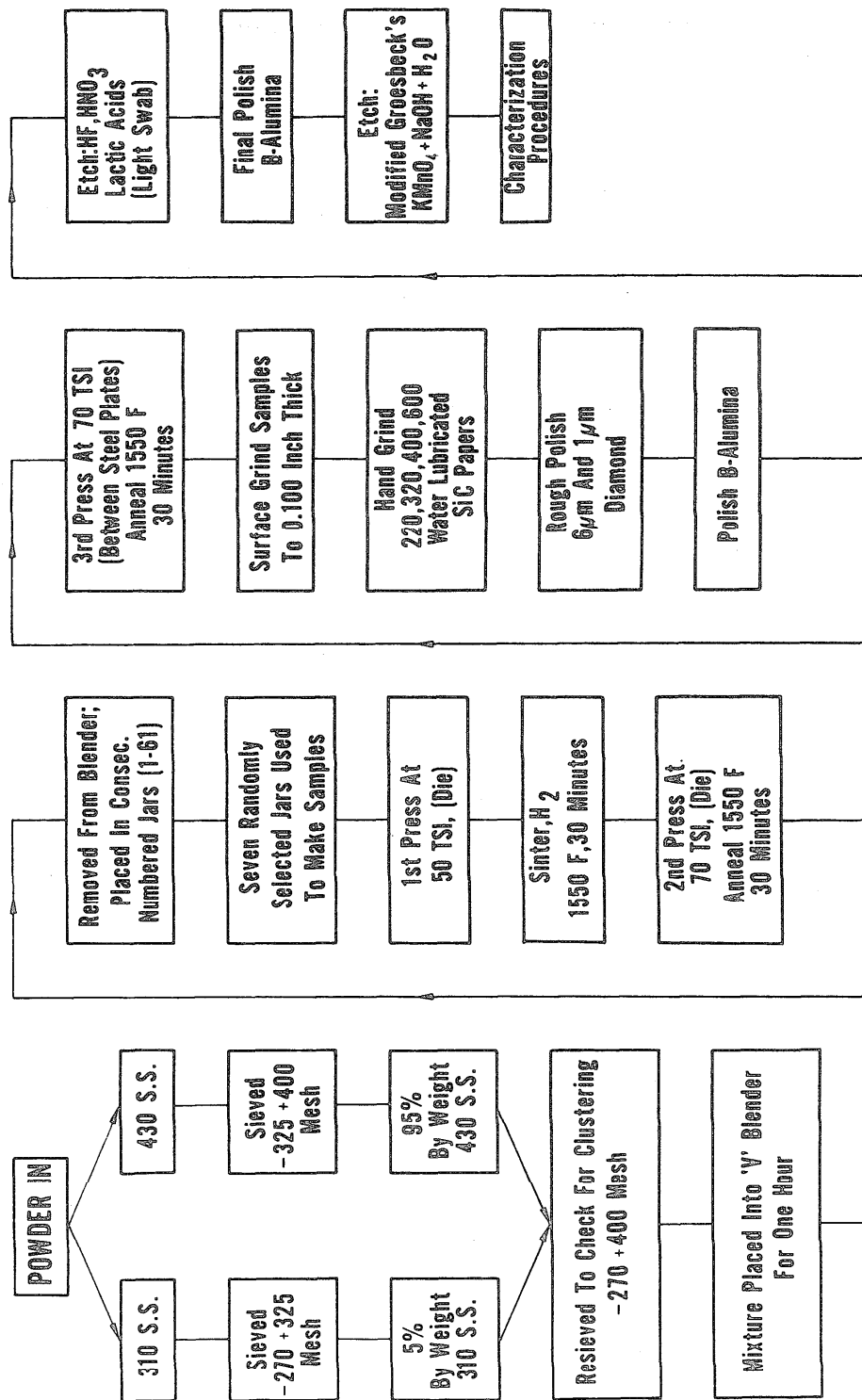
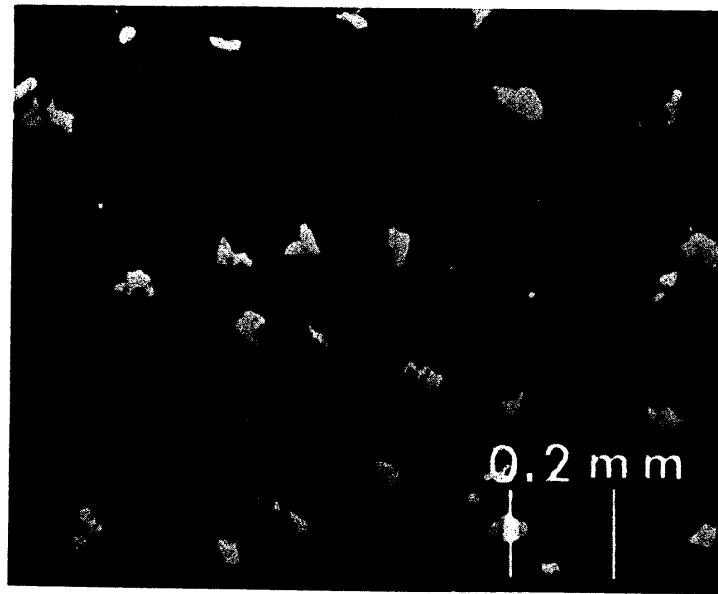
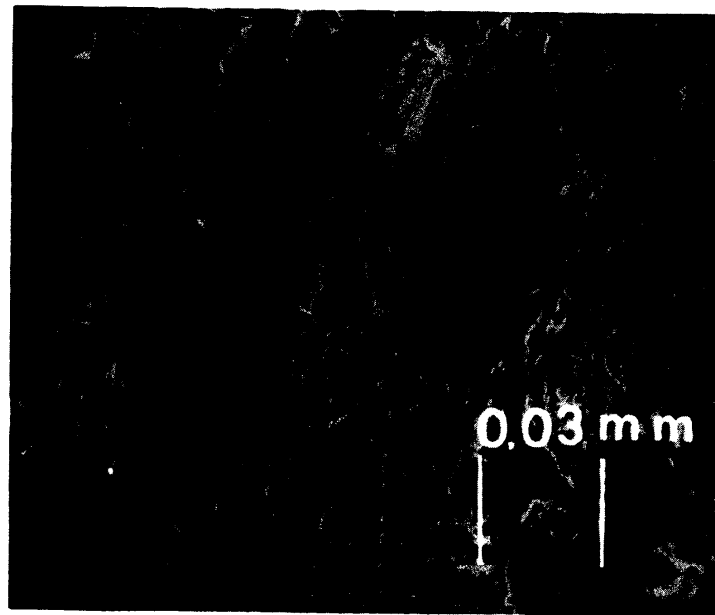


Figure 2. Fabrication steps for SRM-485.
(One TSI = 2000 lb/in.)



a



b

Figure 3. Structure of finished compacts - etched.
 a. Optical micrographs showing austenite (white) and ferrite (black).
 b. Scanning electron micrograph showing sharp delineation between large austenite particles and ferritic matrix.

the 310 particles are large islands in a matrix of ferritic material. Scanning electron microscopy shows that there is a sharp delineation between the austenitic particles and the ferritic matrix as is evident in figure 3b. Modified Groesbeck's etchant (sample immersed in boiling etchant of 30 g KMnO_4 , 30 g NaOH , and 100 ml distilled H_2O) covers the ferritic material with a friable layer of what is perhaps a mixed oxide while the austenite is unaffected. The final compact then appears as a dark brown ferritic matrix with randomly placed austenite particles and some pores.

A section through one of the compacts is shown in figure 4. No important agglomeration of austenitic particles is seen throughout the section. However, it is clear that random cuts within the section may yield different percentages of austenite when a single surface is characterized - as is done in X-ray diffraction or optical microscopy. Consequently, one face of each specimen was characterized and that face only is certified with respect to its austenite content.

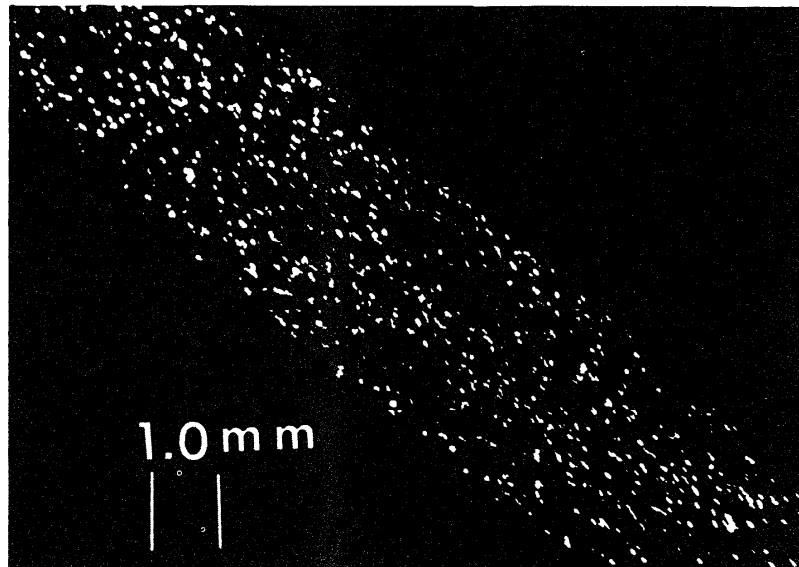


Figure 4. Cross-section of typical compact.

CHARACTERIZATION OF SRM-485

There is virtually no nickel in the ferritic powder while the austenitic powder contains 20.4 percent nickel by weight. Therefore, if there is no diffusion of nickel into the ferrite during the fabrication process, X-ray fluorescence analysis for the nickel content of the compact can be used as a direct measure of the austenite content. For X-ray fluorescence analysis to be successful however, a set of standards is required to calibrate nickel (austenite) content versus X-ray intensity.

The electron probe microanalyzer was used to determine whether or not any diffusion of nickel into the ferritic matrix had occurred. The microprobe operating voltage was 20 kV and the Ni-K α peak was monitored with a LiF crystal-sealed proportional detector system. About fifteen separate austenite-ferrite interfaces were examined. The nickel count rate in the austenite was approximately 4500 counts/second. A typical trace through an austenite particle is shown in figure 5. The nickel signal goes from near zero (ferritic) to full signal (austenitic) in a space of about 3 μ m. This value is approximately the spatial resolution of the X-ray signal from the microprobe. No measureable diffusion of nickel into the ferritic matrix was observed. Also it was noted that the nickel content within a given austenite particle and from particle-to-particle was nearly constant.

To establish the X-ray intensity versus nickel (austenite) content calibration curve, five special powder compacts were prepared. These nominally contained 0, 10, 15, 20, and 25 percent austenite. One of the compacts to be certified was also picked for this purpose. Except for the completely ferritic specimen, these compacts were evaluated by quantitative microscopy to determine their austenite content. The same austenite compacts also were examined by X-ray diffraction (1).

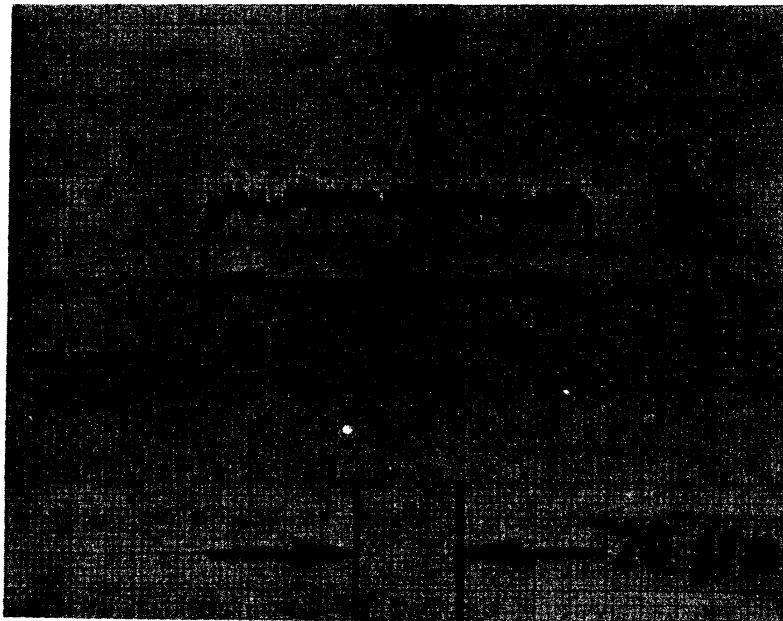


Figure 5. Strip-chart recording of Ni-K α signal vs. position in microprobe trace: a = Ni-signal in austenite particle, b = Ni-signal in ferritic matrix, c = Ni-signal at austenite-ferrite matrix. Full scale about 10,000 counts/second.

Quantitative microscopy could be used because the modified Groesbeck's etchant provides a complete color separation of the austenite (white) and ferrite (brown). Thus, the percentage white phase (austenite) can be determined provided a porosity correction is made. Since the pores are "black" the porosity correction readily can be made. The porosity of the specimens averages about five percent.

Two quantitative microscopy devices were used to characterize the calibration specimens: a high-precision NBS drum-scanner (2); a quantitative television microscope, (QTM). The NBS drum-scanner required 203 x 254 mm (8 x 10 in.) high contrast micrographic prints as input. Final magnifications were at 125 diameters. Thus, a region 1.62 x 2.03 mm

on the specimen was examined. Five such areas were chosen for each specimen which is only about five percent of the total area of the specimen.

By means of the QTM, more than 95 percent of the surface could be sampled. In the QTM, an image of the actual specimen is observed on a television monitor. The QTM then reads percentage white, i.e., austenite in that field. The working frame size on the monitor is 198 mm x 225 mm and the specimen image is magnified 198 diameters. Under these conditions, 80 fields cover almost the entire surface. The average of the 80 austenite determinations gives the austenite percentage on the surface. Care is taken so that successive areas do not overlap.

Extensive tests over a period of two months using three different operators indicated that QTM drift was not a serious problem. However, the absolute white-black threshold did seem to vary with time and operator. Exhaustive studies of a previous set of four compacts having a nominal austenite content of 5 percent indicated a standard deviation of 0.23 percent.

The drum-scanner is far more precise than the QTM but the scanner samples only 5 percent of the surface. Hence, in establishing the calibration curve for X-ray fluorescence, the drum-scanner and QTM values are given equal weight. Table 2 gives the results.

Table 2. Determinations for Establishing X-ray Calibration Curve of Figure 6.

Method \	Nominal	5	10	15	20	25
	Austenite Weight Percentage					
Drum scanner		-	8.83	15.37	19.04	31.44
QTM		4.90	10.04	16.04	18.05	27.11
Calibration curve value		4.90	9.6	15.7	18.0	29.8
X-ray diffraction		4.8	9.4	16.0	17.6	28.3

The calibration curve established with the results in table 2 is shown in figure 6. The equation of the least squares fitted curve is:

$$C_{Ni}(\%) = -0.0332 + 2.687 \times 10^{-4} I + 3.156 \times 10^{-8} I^2 - 1.21 \times 10^{-12} I^3 \quad (1)$$

where I is the Ni-K α signal in counts per second.

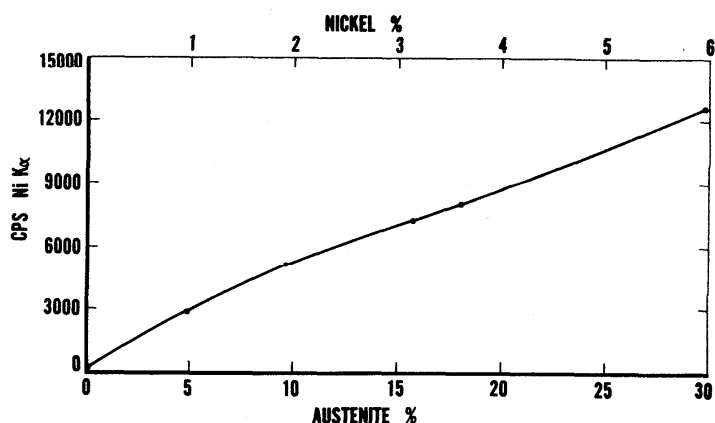


Figure 6. Calibration curve for X-ray fluorescence analysis characterization of SRM-485.

At low nickel (austenite) values, a definite departure from linearity exists. We believe that this is due to the pronounced grain size effect caused by having discrete nickel X-ray emitters scattered throughout the surface. These emitters vary considerably in size and distribution as the absolute nickel content increases. Claisse and Samson (3) have discussed similar effects. Because of this specific nickel distribution, more nickel intensity is observed than would be the case if the nickel were in solution in an iron-base matrix. The X-ray self absorption is considerably reduced by concentrating the nickel into discrete particles in the matrix.

Equation 1 was used to establish the nickel content and hence the austenite content of all 134 specimens. The X-ray fluorescence results were obtained on two different days, but all samples were run at least once on each day. The X-ray results are based on three determinations of Ni-K α count rate. Standards were rerun approximately once every 90 minutes. No significant drift of the X-ray fluorescence unit was noted.

The operating conditions were as follows:

X-ray tube: Tungsten
Crystal : LiF
Voltage : 44 kV
Current : 44 ma
Detector : Scintillator @ 1000 volts
Collimator: Fine

Specimens were placed in an air path. The primary X-ray beam nearly irradiated the entire specimen face.

As a final test, fifteen specimens were run individually on the QTM. The comparison of X-ray and QTM results is shown in table 3. The agreement is considered satisfactory.

Table 3. Comparison of QTM and X-ray Fluorescence Results.

<u>Specimen Number</u>	<u>QTM^a Results</u>	<u>Std. Error QTM</u>	<u>X-ray^a Results</u>	<u>Std. Error X-ray</u>
5	3.9	0.32	4.2	0.01
9	4.0	0.02	3.7	0.03
19	4.4	0.04	4.0	0.01
21	3.8	0.24	3.7	0.02
42	4.0	0.28	4.0	0.01
49	4.4	0.34	3.8	0.01
69	4.7	0.37	4.2	0.02
71	5.4	0.40	4.6	0.03
80	4.4	0.27	4.0	0.04
81	3.5	0.17	3.9	0.01
86	3.3	0.22	4.2	0.05
117	3.1	0.36	3.2	0.08
119	3.5	0.30	3.6	0.04
128	5.0	0.41	4.4	0.04
141	4.6	0.51	4.2	0.05

^aGiven in percent austenite.

To show the overall distribution of the results, a histogram of number of samples versus austenite composition was plotted for the entire population of 134 specimens as shown in figure 7.

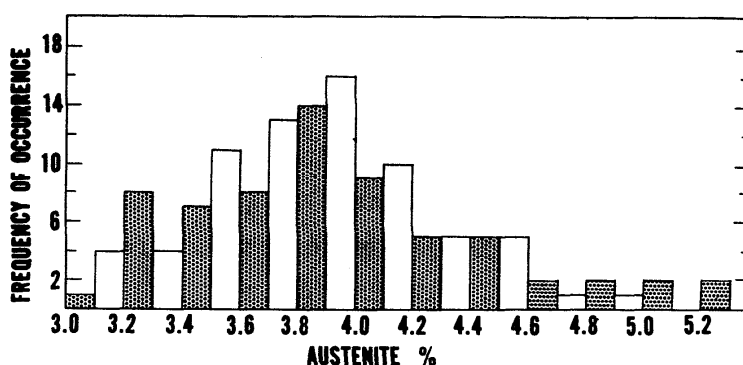


Figure 7. Number of samples in each composition range from 3.0 to 5.3 percent austenite. The total population of 134 standard samples is represented.

CONCLUSIONS

SRM-485 is satisfactory for issuance as a standard for X-ray diffraction determination of retained austenite at the 3 to 5 percent austenite range. In special cases, SRM-485 also may be used as an X-ray fluorescence standard for determining the nickel content in nickel-iron or nickel-chromium-iron composites.

SRM-485 should not be used as a standard for quantitative microscopy. For single field determinations, too few austenite particles are present for statistically meaningful results. Average values for many fields often give unacceptably large standard errors as shown in table 3.

In using SRM-485 care must be taken not to alter the certified face.

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REFERENCES

- [1] Ogilvie, R. E., Retained Austenite by X-rays, Norelco Reporter, VI, 3, 60 (1959).
- [2] Moore, G. A., Automatic Scanning and Computer Processes for the Quantitative Analysis of Micrographs and Equivalent Subjects, Pictorial Pattern Recognition, p. 275 (Thompson Book Co., Washington, D. C., 1968).
- [3] Claisse, F., and Samson, C., Heterogeneity Effects in X-ray Analysis, Advances in X-ray Analysis, 5, p. 335, (1962).