Standard Reference Materials:

A STANDARD REFERENCE MATERIAL CONTAINING NOMINALLY FIFTEEN PERCENT AUSTENITE (SRM 486

C. G. Interrante and G. E. Hicho

National Measurement Laboratory
National Bureau of Standards
Washington, DC 20234

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

Issued January 1982

Library of Congress Catalog Card Number: 81-600173

National Bureau of Standards Special Publication 260-73
Nat. Bur. Stand. (U.S.), Spec. Publ. 260-73, 34 pages (Jan. 1982)
CODEN: XNBSAV

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 1982

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402
Price
(Add 25 percent for other than U.S. mailing)

PREFACE

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards are well-characterized materials produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system are carried out through the mechanism and use of SRM's. For many of the Nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series, is reserved for this purpose.

This 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification, and use of NBS-SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. These papers also should provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the authors. Other questions concerned with the availability, delivery, price, and so forth will receive prompt attention from:

Office of Standard Reference Materials
National Bureau of Standards
Washington, D.C. 20234

George A. Uriano, Chief
Office of Standard Reference Materials

TABLE OF CONTENTS

	Page
ABSTRACT	1
INTRODUCTION	2
GENERAL DESCRIPTION OF SRM	3
PREPARATION OF THE COMPACTS	4
PREFERRED ORIENTATION	11
CHARACTERIZATION OF SRM 486	12
COMPARISON OF DIFFRACTION AND FLUORESCENCE RESULTS	22
CONCLUSIONS	25
ACKNOWLEDGMENTS	25
REFERENCES	25

LIST OF TABLES

		Page
1.	Chemical Analysis of Stainless Steel Powder Particles	4
2.	Comparison of X-Ray Diffraction and X-ray Fluorescence Measurements of Austenite Content for Six Specimens	23

LIST OF FIGURES

		Page
1.	Scanning electron micrographs of the powders	5
2.	Fabrication and inspection of powder compacts	7
3.	Appearance of as-polished compacts	10
4.	Characterization procedures for SRM 486	13
5.	Structure of etched compacts	17
6.	Two compacts, as etched with modified Grosbeck's reagent	18
7.	Calibration curve showing percent austenite by volume as a function of nickel-K_α counts	20
8.	Histogram showing frequency of occurrence vs. austenite content, for 162 certified copies	21

A Standard Reference Material Containing Nominally Fifteen Percent Austenite (SRM 486)

C. G. Interrante and G. E. Hicho

Fracture and Deformation Division
Center for Materials Sciences
National Measurement Laboratory
National Bureau of Standards
Washington, D.C. 20234

ABSTRACT

This Standard Reference Material, SRM-486, is intended for the calibration of x-ray diffraction equipment used in determining the amount of retained austenite in ferrous materials. It was produced using powder metallurgical techniques and known amounts of type 310 stainless steel powder (austenitic) and type 430 stainless steel powder (ferritic) to make a blend of 15 percent by weight (14.7 percent by volume) austenite in ferrite. From a larger blend of these powders, powder for 174 compacts was taken. Using 12 of these compacts, a calibration curve was established for the certification of the remaining compacts. The curve relates the nickel x-ray count rate of x-ray fluorescence measurements to the volume percentage of austenite as determined by quantitative microscopy measurements of area percentage. The austenite content of this SRM can be related directly to the nickel count rate, because the nickel content of the austenitic powder (20.9 weight percent) is many times that of the ferritic powder (0.10 weight percent). The mean percentage austenite for 162 certified standards is 14.7 volume percent; this value exactly equals the volume percentage of austenite powder in the original blend. X-ray diffraction determinations of the austenite content are in good agreement with the certified content of austenite. The SRM may be used as an x-ray diffraction standard for austenite or, in special cases, as an x-ray fluorescence standard for nickel content.

Key words: Austenite in ferrite; austenite standard; electron microprobe; powder metallurgy; quantitative microscopy; Standard Reference Material; x-ray diffraction; x-ray fluorescence analysis.

INTRODUCTION

This Standard Reference Material has been produced to provide a means for calibration of x-ray diffraction equipment. Standard Reference Materials that contain known proportions of austenite in ferrite are required to assess the experimental and computational techniques that are used in x-ray measurements of the austenite content of ferrous materials. The austenite is present in ferritic steels because it is sometimes retained in martensite that forms after quenching from the austenitic region. The amount of this retained austenite can critically affect properties, fabricability, or service performance. Thus, sometimes it is necessary to quantitatively establish the austenite content. Measurements of the percentage austenite in ferrous materials are made using a series of x-ray diffraction lines using a complex process that requires judgment in the application of correction factors for the effects of various material factors and instrumental parameters. Thus, an austenite determination is not made from first principles alone, and this Standard Reference Material can be a useful aid in the determination.

In a reference material used for these measurements, it is desired to have reasonable homogeneity and a minimum of metallurgical confoundments, such as residual stress, preferred orientation, large grain size, and twinning. To meet these requirements, the National Bureau of Standards is in the process of producing a series of Standard Reference Materials (SRM's) containing various percentages of austenite in ferrite. The first of these SRM's was issued in July of 1970 as SRM 485; it contained a nominal 4 percent austenite [1]. Both SRM 485 and the current issue, SRM 486, which contains a nominal 15 percent austenite, were prepared by means of powder metallurgical methods.

The purpose of this report is to describe the methods used in the certification of the austenite content of the surface of each of 162 compacts prepared for use as SRM 486. For each compact, a separate characterization of austenite content is required, because complete homogeneous blending (of the austenite and ferrite powders used to make the compacts) cannot be achieved to the degree required for this SRM. For this same reason, the certified value of each compact is valid only for the certified surface.

GENERAL DESCRIPTION OF SRM

This SRM contains two structurally different constituents that are highly stable and require substantial changes in chemical composition to affect a transformation of the structure. The constituents are a fully austenitic type 310 stainless steel powder (austenite) and a fully ferritic type 430 stainless steel powder (ferrite). The austenite contains large amounts of nickel and chromium that render it austenitic, even at nickel concentrations significantly below the 20 percent level of the nominal composition for type 310 stainless steel. The ferrite contains large amounts of chromium, but almost no nickel. Much larger concentrations of nickel would be required for this composition to become austenitic at room temperature. Hence, significant amounts of nickel diffusion could occur, during annealing or sintering of powder compactions of these two constituents, without causing any significant amount of transformation to alter the structure of either constituent.

This SRM was prepared from a blend of the austenite and ferrite powders. The powders were compacted by various pressing and annealing treatments. The compacts are 21 mm (0.83 in.) in diameter with a 2.4 mm (0.094 in.) thickness. One surface is polished, and this surface has been characterized with respect to austenite content. The lowest actual percentage austenite in the certified faces of these unetched SRM's is 13.4 percent, and the highest value is 16.9 percent[1]. The mean for 162 SRM's prepared is 14.7 volume percent. These compacts were taken from a larger blend of the powders that contained 14.7 volume percent (15.00 weight percent) austenite.

Care should be taken to avoid alterations of, or damage to, the certified surface. Research conducted on methods for preparation of this SRM has shown that alterations of the surface can render the SRM useless, as for example: (1) Etching procedures have been shown to increase the nickel counts in x-ray fluorescence measurements by as much as 12 percent of the amount present; and (2) metal removal by grinding was shown to change the austenite content of the surface by as much as 5 percent of the amount present.

In the above "grinding" example, a controlled experiment was conducted on 23 compacts, using quantitative microscopy (QM) methods to assess the austenite content. Metal was systematically removed from the characterized surfaces of each of the 23 compacts. This was accomplished by hand-grinding and polishing to uniformly remove a

---

[1] The SRM's with certified values outside of the range 13.8 to 16.2 were retained for use in research at NBS.

layer of only 0.08 mm (0.003 in.) of metal. Each compact was then characterized again. The resulting change in the austenite content for a single compact ranged from -4 to +5 percent of the amount present (-0.6 to +0.8 percent austenite). The mean change in austenite content for the 23 compacts, after removal of this small amount of metal, differed by only 0.05 percent austenite (final mean less original mean). However, the above noted changes observed in individual compacts are significant--these changes are due to inhomogeneities in the austenite powder compacts. The measured change in austenite content for the 23 compacts has a standard deviation of 0.40 percent austenite, which equals 2.7 percent of the average amount present. These values are significantly greater than estimates of the precision based on duplicate measurements: 0.45 percent relative (0.067 percent austenite). Thus, the certified value does not apply if the certified surface has been altered or damaged.

PREPARATION OF THE COMPACTS

The austenite and ferrite used to produce the compacts are stainless steel powders produced by water atomization. As shown in Fig. 1, the powders are irregularly shaped and uniformly sized. The figure gives scanning electron micrographs of each type of powder. Figs. 1a and 1b, respectively, represent the type 310 and 430 stainless steel powders, taken at a magnification of 160X, that were used to make the compacts.

Preliminary sizing was done by the producer of the powders and final sizing was done with sieves at NBS. The austenitic powder was passed through a 270 mesh screen and was retained on a 325 mesh screen. This sieving furnished particles in the size range of from 53 to 44 micrometers. Similarly the ferritic powders were sized (-325 to +400 mesh) to furnish particles of 44 to 37 micrometers. The chemical analysis of the powders is given in Table 1.

Table 1. Chemical Analysis of Stainless Steel Powder Particles (content in weight percent).

Elements	310 Stainless Steel	430 Stainless Steel
Chromium	25.43	16.19
Nickel	20.91	0.10
Iron	bal	bal
Carbon	0.03	0.04
Manganese	.14	.04
Phosphorus	.010	.004
Sulfur	.006	.006
Silicon	.98	.53
Molybdenum	.02	.02
Copper	.04	.02

a

b

Figure 1. Scanning electron micrographs of the powders. a. As-sized, type 310 stainless steel powder (fully austenitic). Magnification: 160X. b. As-sized type 430 stainless steel powder (ferritic). Magnification: 160X.

Each step in the preparation of the compacts is shown in a flow diagram given as Fig. 2. Initially 11.4 kg (25 pounds) of the powders were mixed in proportions representing 15.00 percent by weight austenite and the balance ferrite.

Fifteen percent austenite by weight was determined to be equivalent to 14.7 percent by volume. This determination was made using measurements of the densities of the starting materials. The density of the austenite and that of the ferrite were measured picnometrically, after compacts of the 310 and the 430 powders were separately melted (into buttons) and rolled. Average densities from measurements taken on three buttons of each alloy were 7.804 $g.cm^{-3}$ for the austenite and 7.643 $g.cm^{-3}$ for the ferrite. Thus, the original blend of powder from which the compacts were taken is a blend calculated to contain 14.7 volume percent austenite in ferrite.

The mixture of 11 kg (25 lb) of the sized powders was blended in a 4-quart "V" blender for a total of 12 hours. This total blending time was accumulated over a much longer period, during which various samples were taken from the blend for research purposes. The remaining blend of 4.95 kg (10.9 lb) of powder was given a final blending for 8 minutes in a 1 1/2-quart twin-shell blender with intensifier pin bars. This amount of powder is optimal for this size blender. This blend was placed in 12 jars. Four jars of this blend were randomly selected for use in pressing a total of 249 compacts for use in the production of SRM 486. However, only 174 of the compacts were actually used to produce SRM 486. The balance had been rejected (mostly for inhomogeneity or physical damage) during preparation and characterization of the compacts. The remaining blended powder, which was contained in the other eight jars, was pressed into compacts and prepared up to, but not including, the final annealing treatment. These compacts will be held in this condition until the demand for this SRM warrants the preparation of additional certified compacts.

Prior to pressing the blended metal powders into compacts, the powders in the jars were made wet with ethyl alcohol, a volatile substance that could be baked out without leaving a residue. This was done to prevent segregation of the powders, on standing, on handling, and on sampling for pressing.

The compacts were pressed and vacuum-heat-treated. This was done in three stages as shown in Fig. 2. Each heat treatment was conducted for 30 minutes at a temperature of 843 ±14 °C (1550 ±25 °F). These vacuum-heat-treatment cycles duplicate the temperatures and hold times of hydrogen heat treatments used earlier [1] in the preparation of SRM 485. The temperatures and times used for heat treatment of compacts for SRM 486 were chosen after considerable effort was directed towards an alternative treatment that involved either higher temperatures, or longer times at temperature. An alternative heat treatment was sought in an attempt to enhance the bonding between the constituents, and thereby to minimize the likelihood that the compacted particles would be removed from the surface of

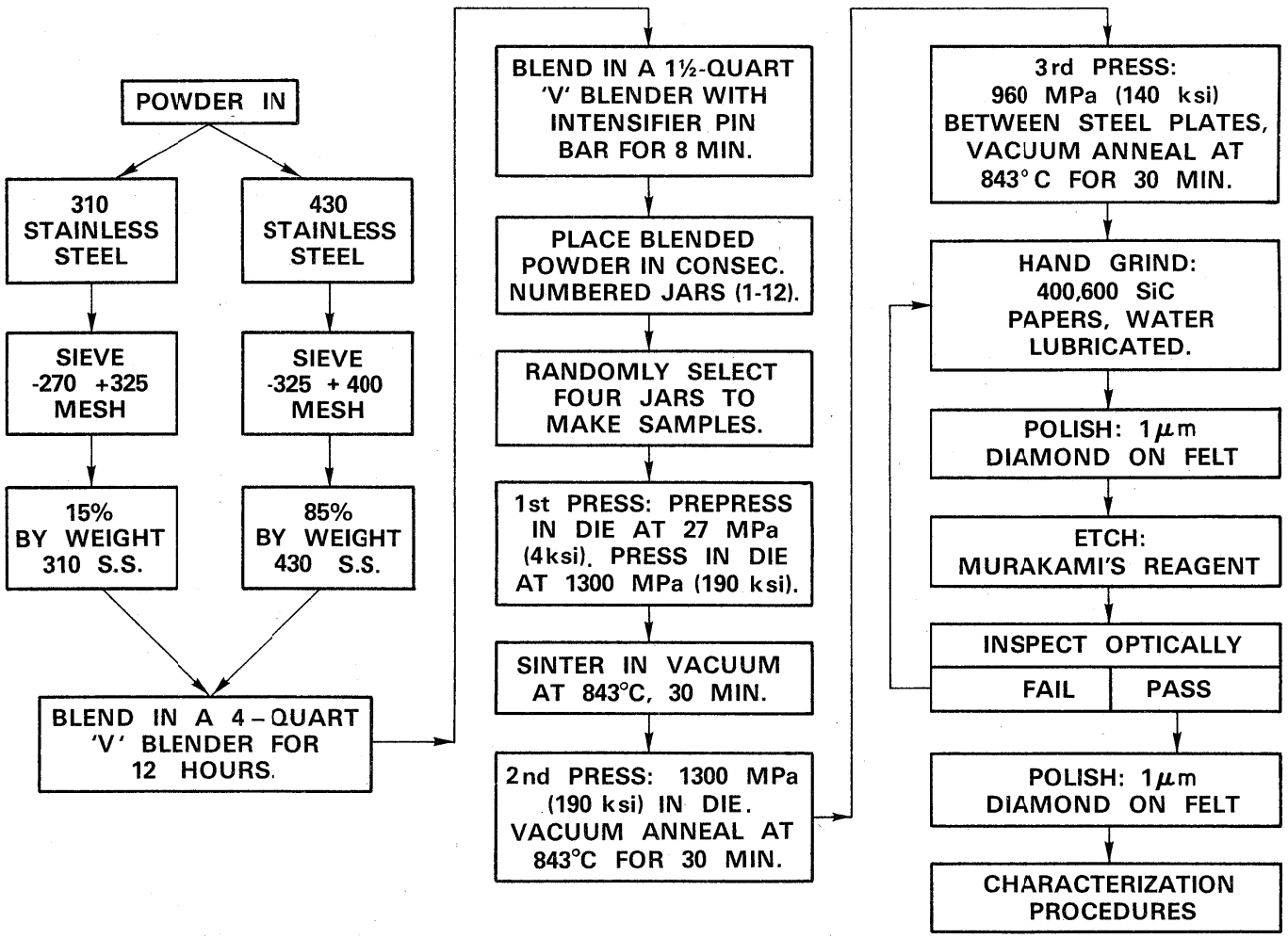


Figure 2. Fabrication and inspection of powder compacts.
(One ksi = 6.89 MPa)

the compact during grinding. In the end, these alternatives were each found to produce levels of nickel diffusion, from the austenite into the ferrite, that might be sufficiently high to alter the austenite content of this SRM.

The alternative heat-treatment cycles were rejected after studies conducted with the electron probe microanalyzer showed that: (1) when the time of each of the three heat-treatment cycles was increased from 30 to 50 minutes and the temperature of only one of these cycles was increased to 871 °C (1600 °F), diffusion of nickel from the austenite was observed to occur at distances of up to 12 micrometers beyond a boundary between particles of austenite and ferrite; and (2) when only the time of each of the three heat-treatment cycles was increased from 30 to 50 minutes, and the temperature was maintained at that used in the earlier work (843 °C), diffusion of nickel was observed to occur at distances of up to 6 micrometers into the ferrite. Thus, with these alternative heat treatments, a nickel diffusion zone of 6 to 12 micrometers could be expected.

In compacts treated using the alternative cycles, the nickel content of the ferrite was only moderately affected over a great majority of the diffusion zone. Nevertheless, for the preparation of SRM 486, it was decided to heat treat at the lower levels of these heat-treatment parameters. Thus, the treatments used are the ones found earlier [1] to give practically no measurable diffusion of nickel, within the limits dictated by the spacial resolution (3 micrometers) of the x-ray signal from the microprobe. Instead, grinding operations, which are done to render the surfaces flat, would all be done by hand to minimize the tendency toward mechanical pull out of particles of either constituent. This was considered to be more acceptable than the use of an alternative heat treatment.

After the three cycles of compaction and heat treatment, compacts were hand ground on wet silicon carbide (SiC) papers, polished on felt using 1-micron diamond paste and a mineral oil lubricant, and etched with Murakami's reagent, using the following technique: The compacts are pre-heated at 130 °C (265 °F) in an oven for 20 minutes. Immediately upon removal from the oven, they are etched with Murakami's reagent. Composition of the reagent is 10 grams potassium hydroxide (KOH), 10 grams potassium ferricyanide ($K_3Fe(CN)_6$), and 100 mL distilled water (H_2O). The reagent is heated to a temperature in the range between 90 and 100 °C (194 to 212 °F). Compacts are removed from the oven individually and swabbed for 2 minutes with the hot etch.

This procedure does not chemically remove very much metal from the polished surface of these compacts. The purpose of the etch is to slightly darken the ferritic phase while leaving the austenitic phase unaffected, so that the austenite particles and their distribution in the ferrite can be inspected optically on the polished and etched surface.

The inspection was performed by two observers, with the intention of eliminating compacts that contain any gross inhomogeneities in the surfaces that were to be certified. Any compact that showed a blemish discernible to either observer, such as a large swirl or any area richer or leaner (in austenite) than its neighborhood, was reprepared. A minimum of 0.025 mm (.001 in.) was mechanically removed from the surface, starting with 400 grit SiC paper. Reprepared compacts were then reinspected. Only those that passed an inspection were further characterized. In this way, gross inhomogeneities in the distribution of austenite over the surface that was to be calibrated were effectively eliminated. After three or four repetitions of this optical inspection procedure, compacts that did not pass inspection were permanently rejected for use as an SRM.

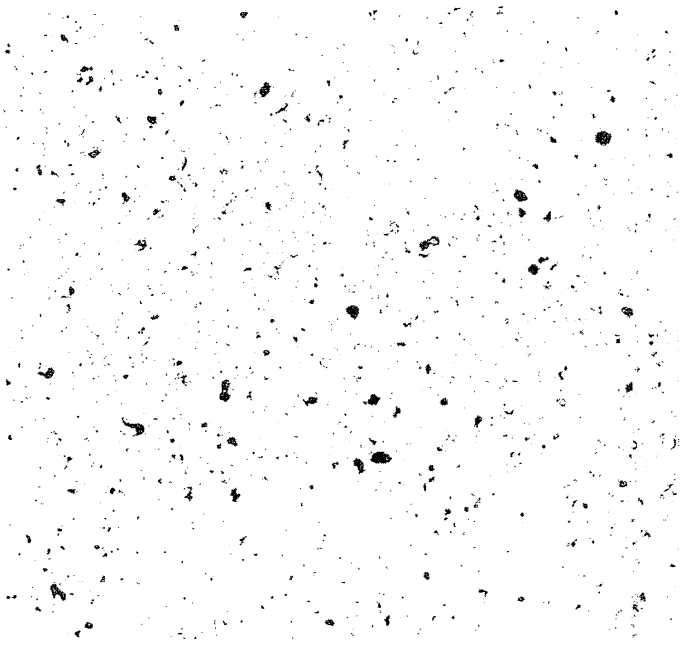
All compacts that passed the optical inspection were polished before being further characterized. Polishing was accomplished with 1-micron diamond on felt with a mineral oil lubricant. This polishing treatment was established as being sufficient to remove all irregularities introduced by the Murakami's etching treatment. For example, porosity was observed to increase slightly by this etchant, and this polishing treatment restored porosity of the surface to its original value.[2]

The appearance of the as-polished compact is shown in Fig. 3. The optical micrograph of Fig. 3a shows the porosity in a region representative of the bulk of the compact. Porosity is greater near the periphery of the compact. The 1-micron diamond polish leaves the edges of the pores well delineated for QM determinations of porosity level. In Fig. 3b, the appearance under the scanning electron microscope (SEM) is shown for a porous region of the surface. In SEM observations, the porosity appeared like that which would be expected from incomplete compaction and no evidence of pull out of particles was observed.

---

[2] Weeping of this reagent (or of reaction products) may occur, particularly if the SRM becomes wet; this will stain the certified surface of SRM 496. This will not affect the accuracy of the SRM. The original unmarred, polished appearance may be restored, without adversely affecting the SRM, by wiping the surface with sterile absorbent cotton dampened with ethyl alcohol or zylene.

a



b

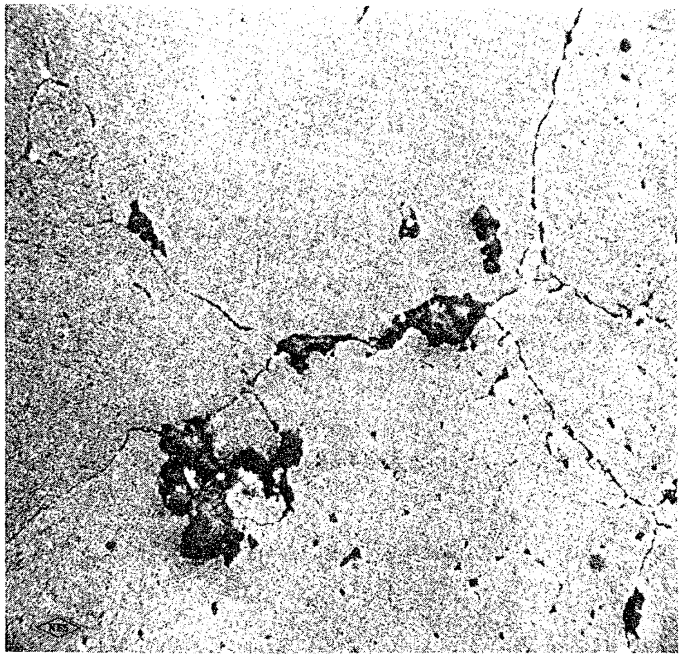


Figure 3. Appearance of as-polished compacts. a. Optical micrograph showing porosity as it would be detected by the QM. Magnification: 40X. b. Scanning electron micrograph showing pores, but no evidence of powder pull out from grinding. Magnification: 1600X.

PREFERRED ORIENTATION

In a material to be used as a reference standard for measurements of retained austenite in steels, it is desirable to have reasonably good homogeneity and a minimum of metallurgical confoundments, such as residual stress, large grain size, twinning, and preferred orientation. Each of these factors was considered in the selection of materials and methods of preparation for this SRM. Six specimen compacts taken from the lot were used to determine whether the thermal and mechanical treatments that were used to prepare the compacts had resulted in an undesirable texture. X-ray diffraction measurements were made using filtered iron radiation. The 110 peak of the alpha phase was monitored during the angular change. In addition, specimen oscillations of 5 mm in its plane (at 67.5 cycles per minute) were used to average grain size effects. These measurements indicated that for five of the six specimens, the observed variations in intensity were consistent with that expected from graininess and not from preferred orientation of crystallographic planes. For the sixth specimen, the observed variations were slightly greater than those for the other five, but here too the level of variation was considered to be within acceptable limits for purposes of this SRM. Further, the results of measurements (discussed later) of the austenite content from integrated intensities of diffraction lines indicated no significant texture. The austenite content, as measured from various pairs of lines, varied within expected limits. Somehow for the sixth specimen mentioned above, this variation was smaller than that observed for any of the other five specimens. It is concluded that any preferred orientation that may exist in these compacts is not sufficient to significantly affect the austenite content as measured using the recommended procedures.

CHARACTERIZATION OF SRM 486

The austenite content of this SRM can be related directly to the nickel content, because the nickel content of the austenite (20.9% Ni by wt.) is many times that of the ferrite (0.10% Ni by wt.). As very precise measurements of the nickel-K_α count rate in x-ray fluorescence (XRF) analyses are possible, this count rate was used to establish the percentage austenite in this SRM. A calibration curve that relates the volume percentage austenite to the nickel-K_α count rate was developed. The percentage austenite was determined optically, using quantitative (television) microscopy (QM), for 12 specially prepared specimens that were statistically selected from the lot of compacts produced for this SRM. The special (etch/stain) preparations used to obtain the QM percentage austenite on these 12 specimens substantially increases the nickel count rate of x-ray fluorescence measurements. Therefore, the calibration curve was established for specimens in the unetched condition, and this SRM is issued in the unetched condition.

The increase in the count rate that occurs on etching can be explained as follows: The etchant reacts with the ferrite at a much greater rate than with the austenite. Hence, the austenite particles stand slightly in relief of the ferrite on the etched surface. This relief interferes with the normal x-ray absorption processes. Those parts of the austenite particles that stand in relief are in the paths of incident, diffracted, and fluorescent radiation to and from the ferrite crystals, and those parts of the ferrite particles that have been etched away no longer occupy positions at which they would have absorbed the radiation to and from the austenite crystals that stand in relief. As a result, the measured diffracted energy from the austenite is intensified. The measured fluorescent radiation from nickel is also intensified, as the nickel content of the austenite is many times greater than that of the ferrite.

The optical percentage of austenite on this same surface is not significantly affected by this etching procedure. As the ferrite is attacked, a thin layer of dark brown reaction products forms wherever the ferrite had been. On the surface of the compact, these products surround the austenite particles and have a detectably different gray level when compared with that of the austenite. The gray level difference is sufficient so that QM procedures can be used to distinguish the austenite from the ferrite. In the relatively unaffected, nearly white austenite, some pitting occurs, but pits that are contained totally within an austenite particle are counted by the QM procedures as though they were "white" austenite. Thus, the etchant increases the x-ray responses of the austenite, but the optical QM response is not significantly affected by the etchant.

Procedures used to certify the percentage austenite in each of 162 compacts are outlined in a flow diagram given as Fig. 4. Each of 174 compacts that passed the optical inspection described earlier were

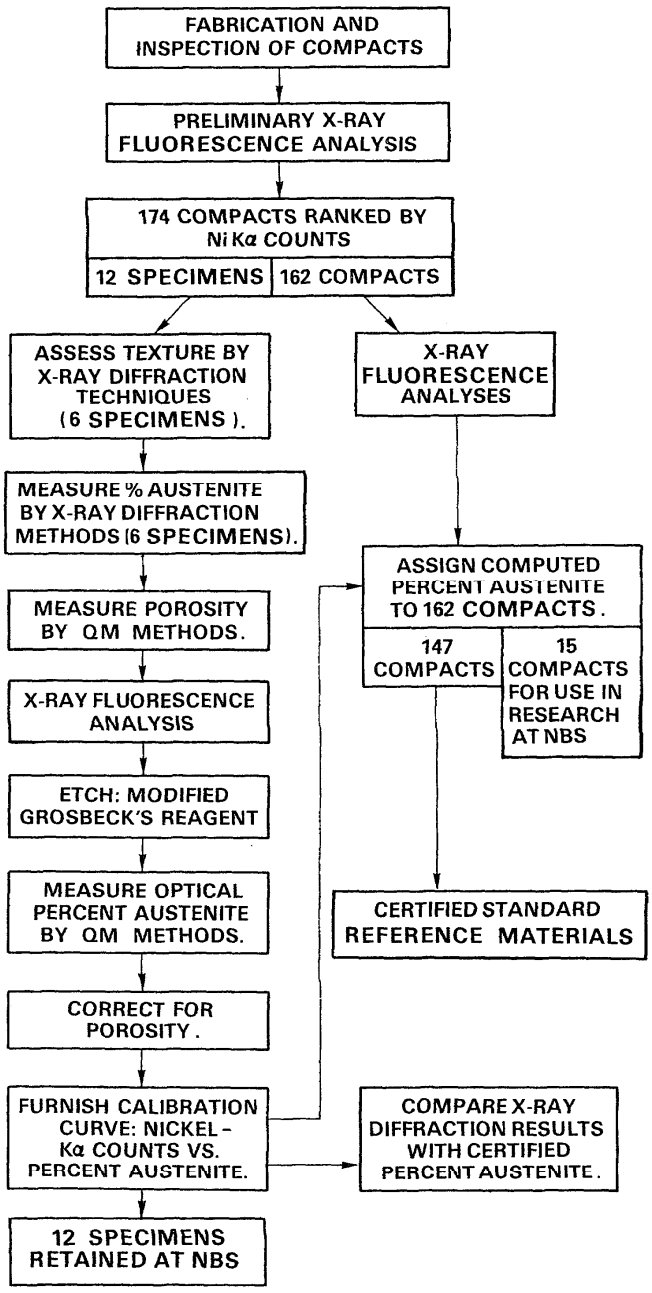


Figure 4. Characterization procedures for SRM-486.

ranked by nickel content using a preliminary XRF analysis of significantly lower precision than that which was used in final analyses. From this ranked set of unetched compacts, a group of 12 specimens were statistically selected for use in the establishment of a calibration curve that relates nickel-K_α count rate to austenite content for specimens in the unetched condition.

Six of 12 specimens were examined for preferred orientation and austenite content, using x-ray diffraction (XRD) methods. Then, for all 12 specimens[3], duplicate porosity measurements were made using QM methods, and additional XRF measurements of nickel count rate were taken. The additional XRF measurements were used to more precisely characterize the nickel content of the 12 specimens before they were etched for use in establishing a calibration curve. The QM porosity content of each sample was used to individually correct the QM determination of austenite content, as discussed later. The XRD determinations of austenite content are compared later with their certified austenite contents, as determined by XRF measurements. The certified content is obtained from a relationship between unetched nickel-K_α counts and QM austenite content. This relationship is referred to as the calibration curve.

The calibration curve was established using the results of the quantitative microscopy (QM) measurements of austenite content and porosity content. Duplicate QM determinations were made, with the second set of measurements being taken after a 90° rotation in the plane of the specimen. The QM techniques were specifically perfected for the characterization of this SRM, with considerable research efforts being directed at the problem. As a result, these QM measurements are believed to be very precise and highly accurate. The precision is reflected by the relative standard deviation, as pooled for duplicate measurements. Based on duplicate measurements of porosity on 12 specimens, this pooled value is 15.7 percent relative (or 0.46 percent absolute). Based on duplicate measurements of the austenite content on 12 specimens, this pooled value is 0.45 percent relative (0.067 percent austenite). The accuracy of these measurements

---

[3] For 2 of these 12 compacts, the percent porosity could not be determined by the QM method. This method rejects a specimen if the "threshold," which is determined for various randomly chosen sites on the specimen, varies beyond prescribed limits. When this rejection occurred, two additional samples were taken from the remainder of the ranked set of 174 compacts (see Fig. 4). These two compacts were used to complete the set of 12 specimens to be etched for use in the establishment of a calibration curve. The two rejected compacts are two on which preferred orientation and austenite content measurements had been performed by XRD methods and they are 2 of 15 compacts retained for use in research at NBS (Fig. 4). This substitution is a detail, which (for simplicity of presentation) is not given in the flow diagram of Fig. 4.

has been verified in several ways. The most cogent verification is the agreement between the mean of the austenite content (14.7 percent by volume) of the 162 certified compacts and the computed nominal austenite content of 14.7 percent by volume of the original blend of powders from which these compacts were taken.

The results of porosity measurements made on the 12 specimens used to establish the calibration curve can be considered to typify the porosity of the lot of certified compacts because the specimens were statistically selected to represent the entire lot. These results indicate that the porosity for these 12 specimens is 2.93 ±0.98 percent.

A single QM determination is a result of measurements taken over 500 fields that represent the central 90 percent of the area of the surface of the specimen. Other measurements taken on fields near the periphery of the specimen (the outer 10 percent of the surface area) could not be used in the determination because their proximity to the periphery of the specimen confounded the measured value. This unavoidable selectivity, in the fields that are counted, results in a determination that is characteristic of the central 90 percent of the specimen surface. For measurements of the austenite content, the number obtained by this procedure adequately represents the entire specimen because the austenite distribution over the entire surface is relatively uniform, with no systematic bias being observed from the center to the periphery of the specimen surface. For measurements of the porosity content, the number is biased on the low side because the outer parts of these compacts are more porous than the central parts, due to the method of compaction. Even this biased measurement of porosity is considered to be an adequate estimate of the porosity of the specimen because only 10 percent of the surface is unexamined and because a large bias would be needed to significantly affect the final result--porosity is used in a correction factor, which is explained later. For example, a very large error of 1 percent absolute in the porosity estimate of a specimen would yield an error of less than 0.2 percent absolute in the determination of the final austenite content of that specimen.

The results of XRF analyses were based on a minimum of six determinations of nickel-K_α count rate for each of the 12 specimens used for the calibration curve. A minimum of three determinations were analyzed for the other 162 compacts. Standards were rerun after 5 to 20 determinations, depending upon the rate of drift of the XRF unit. Drift corrections were made whenever the count rate exceeded predetermined drift limits. In addition, in a computer analysis of the data, the raw data for each set of measurements was drift corrected and normalized, using an internal standard having a predetermined mean value (107,450 counts). The operating conditions were:

X-ray tube - Platinum
Crystal - LiF
Voltage - 39 kV
Current - 34 ma
Detector - Pulse height discriminator at 1650 volts
Collimator - Fine
Gain - Coarse 1/4, fine 1
Count - 30 s in air.

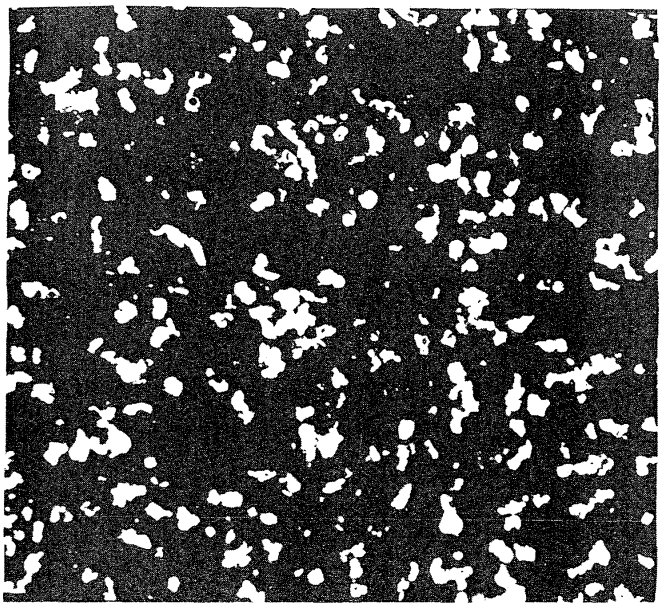
While the compact was spinning, the primary x-ray beam irradiated nearly the entire face of the compact, except for a narrow band (near the circumference) that was blocked out by the holder (fixture). The average of three or more determinations of nickel-K_α counts computed for every compact in the certified lot is within the range 0.87×10^5 to 1.1×10^5 counts. The standard deviation among these normalized determinations for a given compact is always less than 740 counts and is typically 400 nickel-K_α counts (0.07 percent austenite).

The 12 specimens selected for use in the calibration curve were etched with a modification of Grosbeck's reagent, which was used to prepare the surfaces of these specimens for QM measurements of the austenite content. The composition of the reagent is 150 grams potassium permanganate, 150 grams sodium hydroxide, and 500 mL distilled water. The reagent is brought to a boil, and specimens are immersed in the boiling reagent. The number of specimens immersed at one time is held constant, at five, so that the potency of the solution is uniformly high for every specimen. Previously rejected compacts were used to maintain five compacts in the bath, as needed to meet this requirement. The total time of immersion for each compact is 20 minutes. To maintain potency throughout the etching period, a fresh solution is prepared after it has been in use for only 15 minutes. Therefore, two solutions are prepared for each set of five specimens.

The appearance of the etched specimen is shown in Fig. 5, which presents two micrographs. The optical micrograph of Fig. 5a shows the austenite as a nearly white phase surrounded by a matrix of dark gray--actually a deep reddish brown--ferrite. The sharp difference in contrast between the two phases in this etched condition permits accurate QM determinations of the optical percent austenite. The scanning electron micrograph (Fig. 5b) shows that sharp delineation exists between the large austenite particles and the ferrite matrix of smaller ferrite particles.

The degree of uniformity in the distribution of austenite is shown in Fig. 6. Two compacts in the etched condition are shown at about three times actual size. While small local areas may appear sparse or rich in austenite content, the distribution of austenite over an entire surface is relatively uniform.

a



b

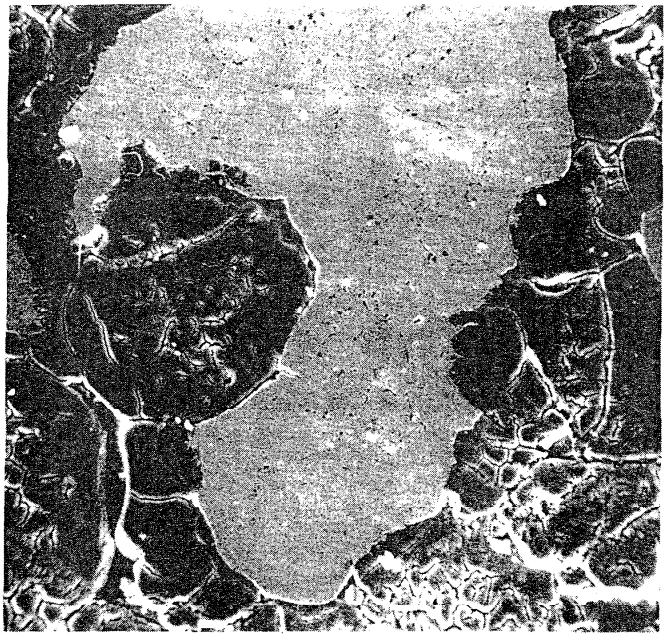


Figure 5. Structure of etched compacts. a. Optical micrographs showing austenite (white) and ferrite (black). Magnification: 40X. b. Scanning electron micrograph showing sharp delineation between large austenite particles and ferritic matrix. Magnification: 800X.

Figure 6. Two compacts, as etched with modified Grosbeck's reagent.
Magnification: 3X

The volume percent austenite was determined from the results of QM measurements of the area fraction of "white" austenite on the surface of each of the etched calibration specimens. To obtain the area (volume) percent austenite for each of the specimens, the optical percentage of the white area is divided by a porosity correction factor, which was determined separately for each of the 12 calibration specimens.[4] The correction factor represents the area fraction of pore-free surface, i.e. (100 -percent porosity)/100.

In earlier research [1] conducted to establish a calibration curve for the certification of SRM 485, it was found that the relationship between nickel-K_α count rate and the percent austenite over the range of from 0 to 30 percent is of the second order, and over the range of from 10 to 30 percent, it is nearly linear. Preliminary analyses of data for the 12 calibration specimens for SRM 486 suggested that the data are linear and extend over a relatively narrow range of 13.4 to 16.9 percent austenite. Therefore, a linear fit was used to describe the portion of the calibration curve that is represented by the compacts certified for SRM 486. The results of a linear regression analysis of the data for 12 calibration compacts are presented as Fig. 7. The QM measurements of volume percent austenite are fitted to the XRF measurements of nickel-K_α counts. The equation of the least-squares-fitted line is:

$$\text{Vol. \% Austenite} = 1.755 \times 10^{-4}\ C - 1.976$$

where C represents nickel-K_α counts taken under conditions stated earlier.

Using this relationship and the normalized results of nickel-K_α counts taken on 162 unetched compacts, the certified percentage austenite was computed for each compact. The distribution of the austenite contents for the 162 compacts is given in a histogram presented as Fig. 8, which shows the frequency of occurrence for 20 austenite-content cells. The certified values (percent) vary from 13.4 to 16.9, with a mean of 14.7 and a sample standard deviation of 0.60 for the 162 observations. The standard error of the mean is 0.05 percent austenite. A total of 15 of these 162 compacts are being retained at the NBS for the development of additional reference materials.

---

[4] It is recognized that a significant random error in the certified austenite content of any given sample is introduced due to variability of porosity in the 162 certified samples. Because this error is believed to be within ±0.2 percent austenite, the porosity level was not measured on each of the 162 certified SRM's.

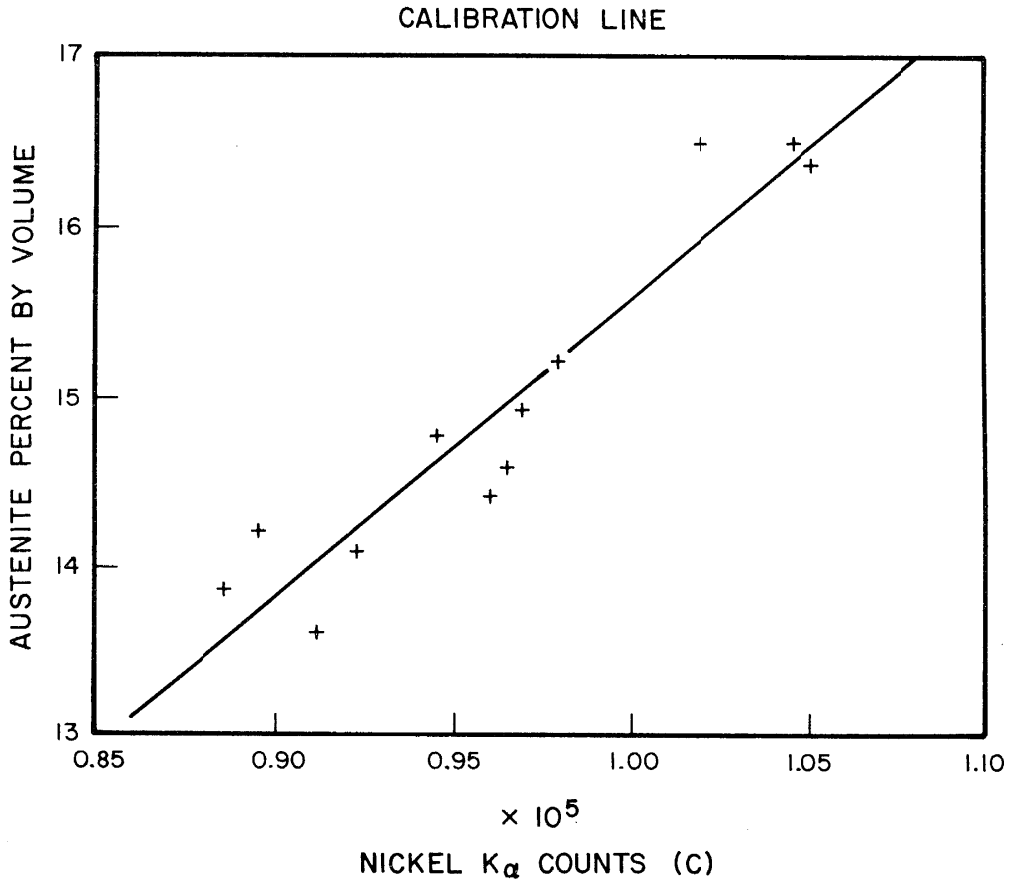


Figure 7. Calibration curve showing percent austenite by volume as a function of nickel-K_α counts.

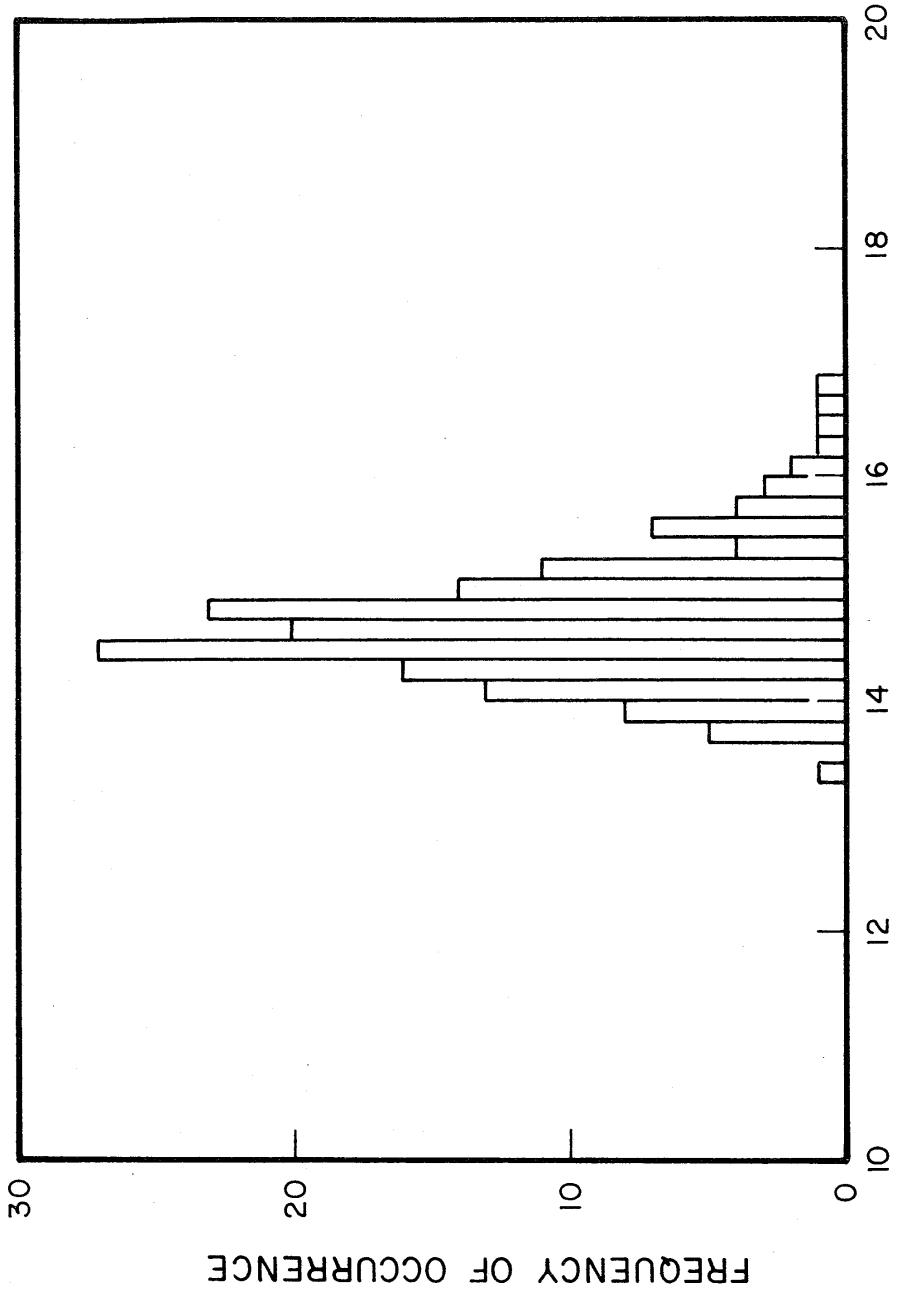


Figure 8. Histogram showing frequency of occurrence vs. austenite content, for 162 certified compacts.

COMPARISON OF DIFFRACTION AND FLUORESCENCE RESULTS

Results of x-ray diffraction measurements of the percentage austenite are shown here to be in generally good agreement with the certified values. The six specimens used in the XRD measurements for preferred orientation, described earlier, are also used here. For this comparison XRD and XRF measurements were conducted with the specimens in the as-polished condition, i.e. before the modified Grosbeck's reagent was applied for QM measurements.

The XRD measurements of austenite content were conducted using methods and recommendations described in NBS TN 709 [2], which recommend that the surface to be analyzed shall be rotated in its plane. The operating conditions were

X-ray tube - chromium
Voltage - 40 kV
Current - 30 mA
Scan rate, 2θ - 1/8 degree/minute
Monochromator - curved oriented graphite
Counting interval - 20 s
Divergence slit - 1 or 4 degrees.

The percentage austenite was computed for each specimen, using measurements taken on three planes (111, 200 and 220) for both the alpha (ferrite) phase and the gamma (austenite) phase. In Table 2, a summary of these results is given under the heading XRD.

Under the heading CV are results of XRF measurements. These values were computed from the regression result of the calibration curve using the normalized nickel-K_α counts taken on each specimen in the unetched condition. The abbreviation CV for certified value is used to represent these results. This is done to acknowledge that the indicated value is the certified value that could have been assigned to the specimen had it not been altered by the etchant used to prepare it for QM measurements.

The table shows that the differences (XRD-CV) range from +0.4 to -1.3 percent austenite (+3 to -8 percent relative), with a mean of -0.21 percent austenite, and the data suggest that systematic bias might exist. At larger values of CV, the difference tends to be more negative. Although it is not shown in the table, the standard deviation for an XRD measurement is of the order of 0.5 percent austenite. Further, it is noted that the austenite (certified) content from fluorescence measurement (CV) is believed to be accurate within ±0.5 percent. Thus, the differences in the table all appear to be within expected limits, except for the specimen with a difference of -1.3 percent austenite.

Table 2 - Comparison of X-Ray Diffraction and X-Ray Fluorescence Measurements of Austenite Content for Six Specimens

	Austenite Content (volume percent)		Difference	
			Absolute	Relative
	CV	XRD	XRD-CV	$\frac{XRD-CV}{CV}$
	13.68	14.00	0.32	0.023
	14.62	15.03	0.41	0.028
	14.89	14.96	0.07	0.005
	14.96	14.48	-0.48	-0.032
	15.92	15.62	-0.30	-0.019
	16.38	15.12	-1.26	-0.077
Average	15.08	14.87	-0.21	-0.012
Std. Dev.	--	--	$\pm$.62	$\pm$0.039

* CV = certified value

For this specimen, the XRD measurement appears to be unexpectedly low. Of course, this was not known at the time that the XRD measurements were taken, as the austenite (certified) contents of these samples were not known until after they had been etched and the calibration curve had been established. Further, the XRD measurements were made without a Standard Reference Material for use in the optimization of experimental and computational techniques used in these determinations. With these considerations in mind, the agreement between the XRF and XRD measurements is believed to be generally good. It is also noted that without the value (XRD-CV) of -1.3, the data set would have an average difference of nearly zero, instead of the suggested biased average of -0.21 percent austenite (-1.2 percent relative).

On the question of the accuracy of the certified value, several factors are considered here on the precision and possible sources of bias in measurements for the certification of this SRM. The CV for each compact is obtained from the calibration curve (which has a residu standard deviation of $s_y = 0.35$) using XRF measurements; a minimum of three determinations of the nickel-K_α count rate is taken. Typically, the standard deviation among these determinations is ±400 counts or 0.07 percent austenite. These XRF measurements are considered to be without significant bias, and their precision is sufficiently high so that the total precision of the certified value is due almost entirely to the precision of the quantitative microscope measurements of austenite content. The precision with which a future data point can be added to this curve is ±0.87% austenite, at the 95% confidence level.

Some possible sources of bias were found not to be significant. These include bias in the QM determinations themselves, which would tend to make the mean for all calibrated compacts different from the 14.7 percent austenite that was actually computed; this number exactly equals the value expected from the weights of the powders that were blended to make this standard. Further, the available data indicates no bias due to the use of etched specimens for calibration of unetched specimens. In addition, it is noted that the porosity of the calibrated surface is different for each compact. By our choice of specimens for the calibration curve, this introduces an error that is considered to be unbiased and random[4]; in essence, the mean porosity of the 12 calibration specimens is the assumed porosity for each compact.

Thus, in the absence of known bias, the accuracy of the certified value is estimated[5] from the precision with which the mean value of a point on the calibration curve is known, at the 95 percent confidence level. These uncertainties are larger near the extremes of the curve than near the mean value of 14.7 percent austenite, but should not exceed ±0.5 percent austenite.

---

[5] This accuracy is computed from data for the 12 calibration-curve specimens using the expressions [3]

$$W = (t_{\frac{\alpha}{2}})\, s_y \left[\frac{1}{n} + \frac{(x_o - \bar{x})^2}{\Sigma (x_i - \bar{x})^2}\right]^{1/2}$$

$$W = (2.18)\,(0.35)\,\left[\frac{1}{12} + \frac{(C_o - \bar{C})^2}{\Sigma (C_i - \bar{C})^2}\right]^{1/2}$$

CONCLUSIONS

SRM 486 is satisfactory for issuance as a Standard Reference Material for x-ray diffraction determinations of retained austenite. The percent austenite for the 162 certified compacts is within the range of 13.4 to 16.9 percent by volume. The mean austenite content for the 162 certified compacts is 14.7 volume percent, a value that exactly equals the computed volume percent of the blend from which powders were taken to produce this SRM. In special cases, SRM 486 also may be useful as an x-ray fluorescence standard for determining the nickel content in nickel-iron or nickel-iron-chromium alloys. In using SRM 486, care must be taken not to alter the certified face, and rotation of the SRM is highly recommended to minimize the effects of inhomogeneities in the distribution of austenite on the certified face of the SRM.

ACKNOWLEDGMENTS

Over a period of 8 years, the authors conducted research to develop the method that was used to produce this SRM. In that span of time, many have contributed to this work. Messrs. D. E. Harne and C. H. Brady have diligently applied their skills as technician and metallographer, respectively. Messrs. R. Frace, R. Dotter and R. Heid of the Patterson-Kelley Company, Inc. did the final blending of the powders in their laboratory in East Stroudsburg, PA. Dr. J. J. Filliben has spent many hours developing computer routines and counseling the authors on statistical problems. Mr. C. J. Bechtold and Dr. W. Ruff have assisted greatly through their measurements and counsel on x-ray diffraction measurements. Dr. George A. Moore assisted in development of methods used for the quantitative television microscopy measurements. Dr. P. A. Pella, Dr. K. F. Heinrich, and Ms. M. Darr conducted the x-ray fluorescence measurements. Mr. S. R. Low handled some of the computational tasks. Finally, Dr. E. Passaglia, over many years, was patient as a Division Chief, offered astute technical advice, and frequently gave his time to problem solving.

REFERENCES

[1] Hicho, G.E.; Yakowitz, H.; Rasberry, S.D.; and Michaelis, R.E.; A standard reference material containing nominally four percent austenite. Spec. Publ. 260-25; 1971 February. 14 p.

[2] Bechtold, C.J., An x-ray diffraction method for determining the amount of austenite in an austenite-ferrite mixture. Tech. Note 709; 1972 February. 14 p.

[3] Walpole, R.E.; Myers, R.H. Probability and statistics for engineers and scientists (2 ed) MacMillan Publishing Co., Inc.; 1978. p. 292.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1982 – 360-997/1914