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AEROSPACE RECOMMENDED PRACTICE

ARP 1313

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Revised

DETERMINATION OF TRACE ELEMENTS IN HIGH TEMPERATURE ALLOYS

1. SCOPE: This recommended practice covers two methods of analysis for rapid and accurate quantative determination of trace elements in alloys having a base of iron, nickel, or cobalt and used at elevated temperatures.

2. DISCUSSION: Various spectrographic and spectrometric techniques have been found satisfactory for determining the presence of trace elements down to and below the amounts permitted by AMS 2280. All of these require close attention to details of procedure to assure reproducible results between laboratories. In the absence of standard reference materials from the U. S. Bureau of Standards, these methods require preparation of the necessary solid or solution standards for comparison; particular care is necessary in their preparation to assure uniformity of composition throughout the standards. In the case of solid standards from which chips are cut, exchange of specimens cut from the standards is recommended to assure that reproducible results are obtained.

3. PREPARATION OF STANDARDS:

3.1 Solution Standards: Prepare the following solutions, using only spectrographically-pure or certified reagent-grade chemicals; pure compounds of known composition may be used provided the weight of each such compound will yield the desired weight of metallic element. Use only distilled deionized water.

3.1.1 Matrix Alloy Stock Solution: Prepare a matrix alloy stock solution for each alloy to be analyzed by weighing appropriate amounts of pure elements or compounds to approximate the composition of the alloy. Final concentration shall be such that all elements will remain in solution and the solution will provide for convenient aliquots.

3.1.2 Trace Element Stock Solution: Prepare fresh 1 part per million (ppm) solutions of each trace element to be analyzed by making appropriate dilutions of stock solutions of pure elements or compounds.

3.1.3 Indium Stock Solution: Weigh 0.1209 g of indium oxide (In_2O_3) into a clean beaker. Add 4 cm^3 of hydrochloric acid (HCl), 5 drops of nitric acid (HNO_3), and 10 cm^3 of water, heat until dissolved, cool, and transfer quantitatively into a 100-cm^3 volumetric flask, and dilute to volume with water. Pipet 4 cm^3 of the 1000-ppm indium solution into a second 100-cm^3 volumetric flask and dilute to volume with 1% hydrochloric acid.

3.2 Solid Standards: Select material of an alloy having a composition similar to that of the alloy or alloys which the standards are to represent and known to have low content of the trace elements of concern. If ingots are used, retain one ingot as a base-line standard. Remelt the remaining material, cast one ingot with no additions, unless an ingot has been retained, and to the remaining melt or melts make additions of high-purity metal of the trace elements of concern to produce a series of standards containing up to two times the maximum permitted amount of each trace element.

4. CALIBRATION OF STANDARDS:

4.1 Solution Standards: Pipet 0.0, 2.5, 5.0, 7.5, 10.0, and 12.5 cm^3 of each trace element stock solution of 3.1.2 into polytetrafluoroethylene (PTFE) beakers each containing the equivalent of 10 cm^3 of 100 g/l matrix alloy stock solution of 3.1.1 and dilute to 50 cm^3. Determine lead, bismuth, selenium, tellurium, and thallium concentrations by nonflame atomic absorption spectrophotometry as in 5.1. For the alternative determination of lead, bismuth, and thallium by the oxide (carrier distillation) method as in 5.2, pipet 0.0, 0.1, 0.5, 1.0, 2.0, and 5.0 cm^3 of each trace element stock solution of 3.1.2 into 100-cm^3 PTFE beakers each containing the equivalent of 2.0 cm^3 of 100g/l matrix alloy stock solution of 3.1.1 and 1.0 cm^3 of the indium stock solution of 3.1.3.

4.2 Solid Standards: Cut specimens from the top, middle, and bottom of each ingot prepared as in 3.2. Abrasively clean the surfaces of each specimen to remove burrs and possible contamination, using silicon carbide paper. Wash off debris with clean water and blow off excess water and debris in an air stream. In lieu of abrasive cleaning, surfaces may be milled and the first chips discarded. Prepare chips for analysis, using an end mill of suitable size and depth of cut (3/8 - 5/8 in. (9.5 - 15.9 mm) diameter and 0.008 - 0.012 in. (0.20 - 0.30 mm) depth of cut recommended). Make sufficient chips to provide the required sample size as specified in Section 5 for the analytical procedure used. Determine the lead, bismuth, selenium, tellurium, and thallium contents by nonflame atomic absorption spectrophotometry. Alternatively, lead, bismuth, and thallium may be determined by the oxide (carrier distillation) emission spectrographic technique.

5. ANALYTICAL PROCEDURES:

5.1 Nonflame Atomic Absorption Procedure for Lead, Bismuth, Thallium, Selenium, and Tellurium:

5.1.1 Weight 1.00 g of chips, prepared as in 4.2, from the material to be analyzed to an accuracy of ±0.01 gram. Transfer the chips to a PTFE beaker and dissolve in a 1:1:1 mixture of nitric acid, hydrofluoric acid, and water, warming as necessary. When dissolution is complete, reduce the volume to approximately 5 cm^3 by evaporation, cool, add about 20 cm^3 of water, and heat to dissolve all salts. Cool, transfer to a 25-cm^3 plastic volumetric flask, and dilute to volume with water.

5.1.2 Establish the atomic absorption spectrophotometer parameters necessary to provide the desired sensitivity, adjusting the hollow cathode lamp or electrodeless discharge lamp to bring it into best coincidence with the nonspecific-background-absorbance-correction system if used.

5.1.3 Pipet into the high-temperature graphite furnace 0.050 cm^3 of each standard solution, except 0.020 cm^3 of the standard solution for bismuth, and of the blank from 4.1. Measure the background-corrected sample absorbance for each at the following wavelengths:

Element	Wavelength Angstrom Units
Selenium	1960
Tellurium	2143
Bismuth	2231
Lead	2833
Thallium	2769

Plot the concentration of each element versus the net absorbance. The curve should be linear in the concentration range of interest and intersect the origin. If the curve is not linear, readjust instrument parameters, sample volume, or both and repeat the procedure.

5.1.4 Pipet, in turn, into the high temperature graphite furnace 0.050 cm^3 of each trace element standard solution for any one element, the blank, and the solution from 5.1.1 of each sample of material to be analyzed and determine the net absorbance of each specimen. Repeat this procedure for the standards and samples for each element, using 0.020 cm^3 of the standards and samples for bismuth.

5.1.5 Plot the concentration of each element in the standard stock solutions versus the net absorbance and read from this graph the concentration of each element in each sample.

5.2 Oxide (Carrier Distillation) Emission Spectrographic Procedure for Lead, Bismuth, and Thallium:

5.2.1 Pipet sufficient matrix alloy stock solution to yield 0.2000 g ± 0.005 of alloy into each of five PTFE beakers containing 1.0 cm^3 of 40 ppm indium stock solution.

5.2.2 Add a sufficient quantity of each trace element stock solution to make standards containing 0, 0.5, 1.0, 1.5, and 2.0 times the allowable maximum of each trace element to be determined.

5.2.3 Weigh, to an accuracy of ± 0.0002 g, sufficient chips, prepared as in 4.2 from either solid standards, from the material to be analyzed, or from both. Transfer the chips to a PTFE beaker and dissolve using hydrochloric acid, nitric acid, or hydrofluoric acid or mixtures of these as necessary for complete disolution. Transfer to a 100-cm^3 volumetric flask and dilute to volume with water. Transfer to a plastic bottle if hydrofluoric acid is used.

5.2.4 Aliquot a 0.2000 g portion of each standard from 5.2.3 and each sample into individual 100-cm^3 PTFE beakers each beaker containing 1.0 cm^3 of 40 ppm indium stock solution.

5.2.5 Cautiously evaporate the contents of each beaker to near dryness. DO NOT ALLOW THE CONTENTS TO GO COMPLETELY DRY. Add 5 - 10 cm^3 of nitric acid and repeat the evaporation to near dryness at least twice.

5.2.6 Quantitatively transfer the contents of each beaker into a platinum crucible, using nitric acid, and evaporate to dryness. Heat the crucibles in a muffle furnace at 950° - 1000°F (510° - 537.8°C) for approximately 15 min. and then in a muffle furnace at 1400° - 1450°F (760° - 787.8°C) for approximately 30 minutes. Cool in a desiccator.

5.2.7 Scrape the residue loose, using a clean metal spatula, and transfer the residue to a tared piece of weighing paper and weigh accurately. Add to the sample an amount of silver chloride-lithium fluoride (11 parts AgCl: 1 part LiF) carrier equal to 10% of the sample weight. Transfer the sample and carrier to a mortar and mix thoroughly by grinding lightly with a pestle. Transfer each mixture to a plastic vial containing two 1/8 in. (3.2 mm) diameter plastic balls and agitate in a mechanical device for at least two minutes.

5.2.8 Weigh a 0.0500 g portion of each powder sample to the nearest 0.0002 g and place into a crater electrode (ASTM S-2 or S-3). Gently pack the charge in the electrode, using a venting tool (See 7.3). Install each electrode in turn in a spectrograph and, using proper techniques for the particular instrument, expose each sample on the photographic plate. After all exposures have been completed, process the plate by standard photographic techniques.

5.2.9 Using a densitometer, determine the intensities of the following lines for the respective elements:

Element	Wavelength Angstrom Units
Indium	2753.80
Thallium	2767.87
Lead	2833.00
Bismuth	3067.00

Also determine the background intensity immediately adjacent to each of these lines, on the lower wavelength side. Subtract the background intensity from the line intensity to obtain the net intensity of each line.

5.2.10 Determine the intensity ratio of lead, bismuth, and thallium in each of the samples and standards by dividing the net element line intensity by the net indium line intensity. Plot the concentration of lead, bismuth, and thallium in the standards versus the intensity ratio for each standard. Draw the best straight line through all the points and use as a daily analytical curve. (Up to two points may be discarded if their deviation is excessive.) When at least 10 daily curves have been obtained, plot an average working curve from all the data used for the daily curves. This average curve may be used for its respective set of standards if all the daily curves fall within a band deviating not more than ±0.00005% (±0.5 ppm) for lead and not more than ±0.00001% (±0.1 ppm) for bismuth and thallium.

5.2.11 Determine the concentration of lead, bismuth, and thallium in each sample of material by measuring the net intensity ratio of the lines for these elements and reading the percentages from the daily analytical curve or the average working curve.

5.3 Chip Procedure for Lead, Bismuth, and Thallium:

5.3.1 Weigh a 0.0500 g ± 0.0010 portion of chips, prepared as in 4.2, from solid standards and from the material to be analyzed onto individual pieces of weighing paper. Add 0.0050 g ± 0.0002 of lithium carbonate directly to each paper. Transfer each sample to a crater electrode (ASTM S-2 or S-3) and gently pack into the cup, if necessary, using a 1/8 in. (3.2 mm) diameter graphite rod.

5.3.2 Also prepare a reference electrode containing lead, bismuth, and thallium in a simple matrix for use in locating the analytical lines in the standards and the samples.

5.3.3 Install the reference electrode in the spectrograph and expose, using proper techniques for the instrument used.

5.3.4 Install the electrodes containing the standards and the material to be analyzed in turn and expose, using one set of standards at the beginning and another set at the end of the plate. Process the plate by standard photographic techniques.

5.3.5 Determine the net intensity of the lines given in 5.2.8 in each standard and plot the percentages of lead, bismuth, and thallium versus the intensity. Prepare daily working curves and average ayalytical curves as in 5.2.10.

5.3.6 Determine the concentrations of lead, bismuth, and thallium in each sample of material by measuring the intensities of the lines for these elements and reading from the daily analytical curve or the average working curve of 5.3.5.

6. PRECAUTIONS:

6.1 Care must be taken to be sure that machining and handling do not contaminate the samples.

6.2 Abrasive cutoff wheels may contain trace elements from a few up to several thousand parts per million. Only wheel types known to be low in trace element content should be used for cutting samples. Samples should not be allowed to contact painted portions of the wheel. Wheels should be identified and used only for preparing samples for these procedures.

6.3 Tungsten carbide tools should be used for milling operations and be restricted to preparing samples for these procedures. Grinding wheels should be restricted to use on tools used for preparing samples for these procedures.

6.3.1 If the restriction on use of grinding wheels is impractical, sharpened tools should be cleaned by immersion in hot 50% by volume nitric acid for 10 - 15 minutes.