MACROSCOPIC X-RAY FLUORESCENCE CAPABILITY FOR LARGE-SCALE ELEMENTAL MAPPING

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ABSTRACT
Compositional information at moderate resolution over many centimeters will be powerful in materials research, not only to validate casting models but also to understand large-scale phenomena during solidification. These elemental differences across a part have a huge impact on materials properties so that identifying variations will help industry immensely with process optimization and quality control. Therefore, a nondestructive method of obtaining spatially resolved elemental compositions over large areas would be very useful. To this end, we have developed an enhanced macro-x-ray fluorescence (XRF) capability in conjunction with IXRF Systems, Inc. (Houston, Texas) to accommodate samples larger than those that typically fit into an XRF instrument chamber. Our system can accommodate samples up to 70 cm x 70 cm x 25 cm, which is unique in that most systems are trending toward smaller micro- and nano-XRF. This system uses a rhodium tube having a maximum power of 35 kV and 100 μA; the detector is a liquid-nitrogen cooled, lithium-drifted silicon detector, and the smallest spot size is approximately 400 micrometers. Reference standard specimens will enable quantitative elemental mapping and analysis. Challenges to modifying the equipment are described. Nonuniformities in the INCONEL 718 system will be shown and discussed. As another example, segregation of niobium and molybdenum in depleted uranium (DU) castings has been known to occur based on wet chemical analysis [inductively coupled-plasma mass spectrometry (ICP-MS)], but this destructive and time-consuming measurement is not practical for routine inspection of ingots. The U-Nb system is complicated because of overlap of the Nb K-alpha line with the U L-beta. Preliminary quantitative results are included on the distribution of Nb across slices from DU castings with different cooling rates. We foresee this macro-XRF elemental mapping capability becoming a valuable asset to the materials industry.

INTRODUCTION
The ability to map compositional information over large distances (tens of centimeters) can be used in many applications. Routine and straightforward measurements of large-scale macrosegregation will have innumerable benefits to the metallurgical community and address a critical barrier to progress. Instead of an assumed ideal uniform average composition, in reality elemental distributions often form across a specimen during cooling that can cause an undesirable final microstructure, leading to unwanted materials properties in the final product and causing part failure. Measuring the existence of compositional inhomogeneities, as well as the conditions under which they form, are key components of process optimization; this paper describes our preliminary efforts to integrate macroscopic x-ray fluorescence (macro-XRF) measurements with our foundry for optimization of casting processes. More importantly, understanding the underlying scientific phenomena allows growth of casting technology beyond trial-and-error experimental work toward modeling and predictive capability. In the long-term, more advanced casting codes could be developed as existing theoretical models mature through validation [Flemings (1974); Mehrabian et al. (1970)].
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In industry, defects in initial castings still limit the alloys and shapes that can be cast. This issue often results in scrap material being produced and resources being wasted. Providing spatially resolved chemical information on well-designed experimental castings through macro-XRF can reveal the important underlying mechanisms, optimize the process, and eliminate defects. Even if a large part or casting has to be cut and cleaned to allow XRF to examine the chemical inhomogeneities throughout the interior of the part, significant time still is saved vs using the alternative techniques: either wet chemical analyses methods or electron microscopy and/or micro-XRF. Both of these techniques are more destructive than macro-XRF (requiring cutting out multiple smaller samples from the larger part) and are necessarily followed by careful reconstruction of a montage of the individual pieces of data. A long, single macro-XRF scan along an entire part simplifies collection of higher-resolution data over larger areas for rapid feedback on quality control and readily maintains orientation.

Scaling-up of the XRF technique is not commonly performed, despite its clear utility, and we were unable to find literature references concerning this topic. In concept, XRF hardware should scale readily, but in practice, the main challenge is maintaining a constant distance between the tube/detector and the sample surface, which may have irregular features or be non-flat. We have been working to address certain issues unique to this instrument, such as determining the optimum beam size for depth-of-field versus resolution of features. Samples will be measured in air without any ability for environmental control, but because we are primarily interested in transition metals and higher-Z materials, this issue was not a concern for our purposes.

**EXPERIMENTAL**

The instrument is shown in Figure 1. Originally, this equipment was built by Sandia Livermore National Laboratory [Krafcik and Brooks (1995)]. The hutch has panels on three sides that are not intended to open routinely, but the fourth uses a roll-up door (manually operated) that allows full access to the sample table. The open side will also make sample changes easy for large specimens that may need mechanically assisted lifting (i.e., forklift or crane). All samples are run in air.

IXRF Systems, Inc., was subcontracted to renovate the instrument, which was originally built circa 1990. The source is a rhodium x-ray tube with maximum operation at 35 kV and 100 μA (Model fX Controller 120, supplied by IXRF), with an IXRF Model 550i for detector electronics; the detector is a liquid-nitrogen-cooled, lithium-drifted silicon detector (Kevex 50mm² x-ray detector cryostat, Model 3701-1090-0575, rebuilt by Max Detector, Middleton, Wisconsin). The x- and y-translation stages (maximum allowed weight of 136 kg, part number ZETA83-135-MO with a new OEMZL4 microstepping drive) are built by Parker-Hannifin Corp. (Cleveland, Ohio). The minimum motor step size is significantly smaller than the beam size; the smallest spot size is approximately 0.4 mm at the sample using a platinum foil aperture. For the current work, this beam size is certainly small enough for the purpose of detecting large-scale elemental differences over large distances (e.g., compositional changes of several weight percent over centimeters). If finer resolution is desired in the future, more attention will need to be paid to controlling stage height/depth of field, e.g., through a feedback loop such as those used in automated machine tools, which use a laser for distance measurements. All electronics and software are also from IXRF. Their program, “Iridium,” controls the stages during data acquisition, runs calibration
routines, and allows quantification of elemental constituents (including fundamental parameters and least-squares). Measurement options include point spectra, line scans, and two-dimensional maps over large areas. The detector and tube are mounted at 45° angles to the sample surface, and an optical camera is mounted perpendicular to that surface (Panasonic digital camera GP-KR212).

Figure 1: Macro-XRF equipment at our facility. Open side has a roll-up door for easy access. (1a) Exterior, with workstation around back. (1b) Interior of hutch.
Samples have been prepared using standard metallographic processes. Slices through the plane of interest were cut from ingots. Because we do not yet have automatic stage height control during a run, samples were flat with parallel sides (or mounted flat) for measurement. For these early studies, the height was set manually by use of a scissor lab jack, and the camera video feed in the hutch allowed quick, real-time focusing to the installed focal length of 10 mm. All INCONEL and MONEL specimens (Ni-based superalloys) were run as-cut, after an acetone rinse was used to remove cutting lubricants. For uranium alloy specimens, mechanical polishing to 1 micron removed any ridges or irregularities from the rough saw cut, and electrochemical polishing (5% phosphoric acid and water; 3 V) was used both to remove any mechanical polishing damage and to examine a fresh surface [Kelly et al. (2006)].

RESULTS
IXRF Systems and Los Alamos National Laboratory (LANL) are still working together on developing quantification standards and techniques. One challenge is that there is peak overlap of the main lines in several alloy systems of interest. For example, Figure 2 shows a spectrum from a U-Nb sample. The Nb K-beta line has no overlap, yet the peak may be too weak for reliable quantification at lower concentrations. Because data collection may require days to cover a large area, we are also working on methods to normalize the peak intensities to the total counts to account for any fluctuations in electrical power/beam current during a period of long data collection. Although this instrument is now being used to run select samples from our foundry and from industry, this novel equipment is still being characterized and adjusted as data are collected and analyzed; thus, this is very much a work in progress.

Element intensity maps show promise for many exciting applications for the macro-XRF instrument by providing qualitative elemental distributions. The first example shown in Figure 3 is a slice from a research casting of INCONEL 718. The layout and orientation of the false-color maps from the sample are such that the metal was poured from the left (the images are rotated 90 degrees). The spots along the centerline are shrinkage voids resulting from the casting process. Data collection time for this map was 22 hours. Beyond the centerline voids, “hot spots” of strong element concentration are clearly visible, which indicates segregation of these elements as the sample was formed, either from poor homogeneity before the casting (i.e., incomplete melting of constituents) or from segregation during the solidification. Such qualitative maps can be used to help identify the process parameters that affect the formation of the elemental segregation, plus optimize final manufacturing parameters for specific alloys and/or casting geometries.
Figure 2: Spectrum from a typical U-Nb sample. U Lα line at 13.61 keV; Nb Kβ line at 18.62 keV.
Figure 3: INCONEL 718 research casting; 34.9 kV/7.9 μA; 0.8 s/pt; 0.6 mm step size; TC 32.

Figure 4: Elemental intensity maps from four plates of commercial superalloys. Upper left shows key. Note the large scale of these data -- the four plates have made a scan area of roughly 60 cm on a side. 34.9 kV/7.9 μA; 2 s/pt; 2.4 mm step size; TC 32.

Figure 4 shows an even larger map from a collection of commercially purchased INCONEL and MONEL plates that were physically placed next to each other. This map demonstrates the large-area capability of this system. The area scanned is 60 x 60 cm (over 2 ft on a side). Although this
map was relatively quick at 24 hours, elemental differences between sample plates are clearly visible. This qualitative map readily shows the elemental differences among the samples and demonstrates the utility of being able to rapidly distinguish compositional differences over large areas using the macro-XRF instrument.

Finally, we looked at several slices of cast U-Nb alloys [Worley et al. (2001)]. Three samples from U-Nb bars were examined that were solidified under different cooling rates. These different cooling rates were achieved by using different metal pour temperatures and different bar thicknesses of the molds. Maps are shown in Figure 5 (the wide end corresponds to the top of the casting). Linescan data (horizontal in Figure 5; left is the hot top, and right is the bottom of the casting) are shown in Figure 6. Slower cooling rates were expected to coincide with more chemical variation due to possible migration of the lighter Nb to the top of the casting. Although differences are slight, this trend was indeed observed. The elemental maps indicate the compositional differences more clearly. The monochrome images in the top of Figure 5 show a detectable difference in the Nb map, whereas the false color images in the lower portion of Figure 5 more clearly show the lower concentration of Nb at the bottom of the casting. The Nb color intensity decreases with decreasing height in the mold, confirming the linescan in Figure 6. Differences along the bottom edge of the map are due to edge effects (the cross section of the bar was almost a parallelogram, such that this bottom edge slopes downward, with a larger working distance) and are not real. Both the linescan and the elemental maps show the segregation of Nb, possibly indicating that the dendrites rich in the lighter element, Nb, float to the top if the solidification time is sufficient to allow this movement. Although it is qualitative (not shown), the data from three bars with different solidification conditions show that the casting with the quickest solidification time has the most relative Nb uniformity from top to bottom of the casting (i.e., the least homogeneous Nb distribution occurred with the slowest cooling). This result has important implications for producing parts with a desired compositional profile. Furthermore, process parameter changes can be investigated to identify optimum conditions to generate reliable, homogeneous castings. The macro-XRF is an ideal instrument for providing this rapid feedback to the foundry on the effects of manufacturing changes on final compositional uniformity.
Figure 5: A representative U-Nb casting slice, with the casting top as the wide end. Element intensities (above) and false color images (below). Settings: 34.9 kV/7.9 μA; 1 s/pt; 0.46 mm step size; 19 h; map size 230 mm x 30 mm, TC 32.

Figure 6: Example of data from a horizontal linescan across a U-Nb bar shown above. Y-axis scale is relative intensity (counts); X-axis is in millimeters.

DISCUSSION AND FUTURE WORK
In summary, we have presented a method for examining chemical homogeneity over large length scales via x-ray fluorescence. Fine, detailed information on concentrations over large areas requires time, but XRF is nondestructive, requires little sample preparation, and can run continuously unattended for extended periods. We foresee that many manufacturing samples could be quickly checked for elemental homogeneity in a quality control setting. Moreover, macro-XRF will be a valuable tool in research to validate casting modeling codes and segregation theories. We continue to work toward accurate and reliable quantification of element intensities. Future modifications to the instrument will improve stage height control and allow for non-flat specimen measurements.

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REFERENCES


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