100% In-Process Compositional Testing Using X-Ray Fluorescence

Digital technologies are transforming industry at all levels. Steel has the opportunity to lead all heavy industries as an early adopter of specific digital technologies to improve our sustainability and competitiveness. This column is part of AIST's strategy to become the epicenter for steel's digital transformation, by providing a variety of platforms to showcase and disseminate Industry 4.0 knowledge specific for steel manufacturing, from big-picture concepts to specific processes.

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A single manufacturer can produce hundreds of different metals and alloys for customers. These customers rely on manufacturers to meet specifications for chemical and physical requirements such as heat resistance, corrosion resistance, strength and workability. X-ray fluorescence (XRF) technology is an essential inspection tool that helps with this process. For instance, positive material identification (PMI) using XRF is common in alloy production, fabrication, verification and research activities. Inspectors often use handheld or benchtop XRF instruments to evaluate the composition of parts on-site with accurate, timely results. They can use these precise results to guide all aspects of the alloy manufacturing process, from verifying incoming materials pre-fabrication, to melting/casting, to quality inspection during important points in the process, including final inspection. With an accurate chemical composition, the user can provide distinct traceability of the part itself or within a material lot, helping to strengthen corresponding quality records. Effectively using XRF in maintenance activities such as PMI can help minimize issues like quality system breaches and material mix-ups.

Understanding how XRF works begins with fluorescence. In general, the term fluorescence is defined as the absorption of radiation by a material that causes radiation to be reemitted at a different energy. XRF applies this principle using x-rays. The XRF technique uses either an isotope or electric tube source to illuminate a sample with x-rays. These primary or "incident" x-rays cause the ionization of atoms in the sample. Ionization occurs when an electron ejects from the inner orbitals of an atom, and another electron drops from an outer orbital to replace it. This causes the emission of a secondary or "characteristic" x-ray. The energies of a characteristic x-ray can be used to identify the elements present in a material, as their intensities are proportional to the concentration of those elements. This type of x-ray fluorescence is known as energy-dispersive x-ray fluorescence (EDXRF). EDXRF instruments can run an elemental analysis test in a few steps. The process starts when x-rays strike the detector in the instrument hardware. The detector connects to a pulse processing interface that generates a spectrum of the sample. This spectrum and its representative x-ray energy peaks are fed into a complex mathematical algorithm using the fundamental parameters method of spectral calculation.[1]

Equipment — For this test, two different Olympus® Vanta™ iX in-line XRF analyzer models with Alloy Mode calibration were used. While both models use a 40 kV x-ray tube to excite the sample and a silicon drift detector (SDD) to acquire spectra, each one has a different anode material in the x-ray tube: one is tungsten and one is rhodium. The rhodium tube model can measure elements as low as Z = 12 (i.e., magnesium) and provide silicon results. It also has a large-area SDD compared to the tungsten tube model. The instruments identify the alloy grade using a pre-loaded, editable library of over 550 common, commercially available alloy grades and their elemental chemistry ranges. These grade libraries are commonly used in PMI programs.[2] The analyzers were tested using an offset

Figure 1

The external envelope features of the Vanta iX analyzer.

Figure 2

The input/output (I/O) ports on the Vanta iX analyzer.

distance of 0, 3, 7 or 10 mm between the faceplate of the instrument and the sample to determine if the distance from the instrument has an effect on analytical performance.

Fig. 1 shows the external envelope of the Vanta iX analyzer.

Process Integration of Generated Data — In addition to its analysis capabilities, the Vanta iX instrument supports Industry 4.0 smart manufacturing practices with hardwired connectivity, Power over Ethernet Plus (PoE+), input/output (I/O) connections for automation, and multiple data export options. These connected devices can transmit the data generated on the process floor to a network folder or engineering resource planning software as soon as the test is completed. The data can also be transmitted to a customer's unique Olympus Scientific Cloud™ (OSC) account.

Fig. 2 shows the I/O ports on the analyzer that support several options for integration. The analyzer can be powered by a 18V DC supply or PoE+. The system control is conducted either from an API web socket interface or customer-supplied programmable logic controller (PLC). There are eight general-purpose input/output (GPIO) pins for Olympus-determined use and eight GPIO pins for customizable commands, enabling many configurable logic outputs to direct production flow based on the test result. A USB port is also available to export or transmit data.

Discussion

The two Vanta iX models were tested with common alloy grades to determine how distance from the

instrument affects alloy chemistry readings. The alloy grades were 316 stainless steel (UNS S31600) and 4340 alloy steel (UNS G43400). Their silicon (Si) performance was monitored using a rhodium tube model that can measure elements Z<22 (i.e., titanium). Given that a customer integration may require their analyzer makes no contact with the sample, distance offset was chosen as the test variable. This application is common when the sample is higher than ambient temperature, moving dynamically or has a curved surface.

Figure 3
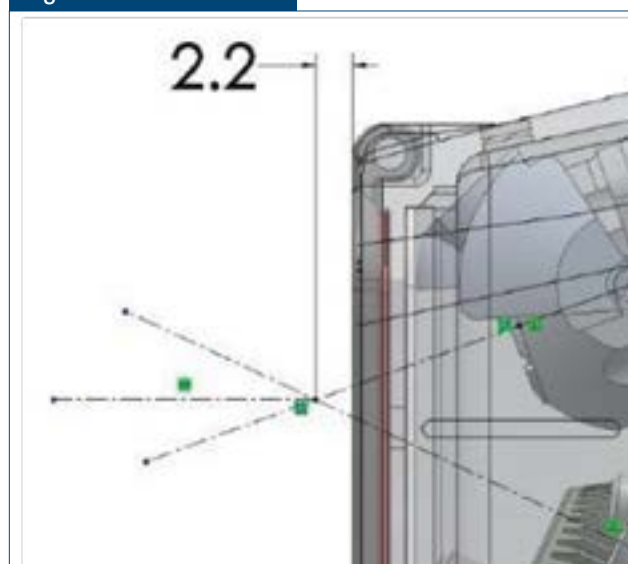
Schematic showing the relative geometry of the Vanta iX analyzer. The focal point is 2.2 mm away from the faceplate.

There are two physical constants with this varying offset: x-ray attenuation in air and the instrument analysis geometry.

As the sample moves farther away from the instrument, elements with less-energetic fluoresced x-rays may see attenuation of these x-rays in air. This physical effect occurs in elements from magnesium to sulfur (Mg–S) in EDXRF and is not unique to the instruments in this study. As x-ray counts become attenuated, fewer counts for that element reach the detector. Fewer counts yield a lower calculated concentration.

The instrument geometry also plays a part in the number of counts that reach the detector. Fig. 3 shows a rough sketch of the tube and detector with relative geometry. The focal point of the x-ray tube is approximately 2.2 mm away from the front plate of the instrument. Samples tested at this distance or closer will see a maximum number of x-rays reach the sample and, consequentially, fluoresce from the sample and travel to the detector.

As the sample moves more than 2.2 mm away from the faceplate, the beam effectively spreads out and becomes less intense as the distance increases. This
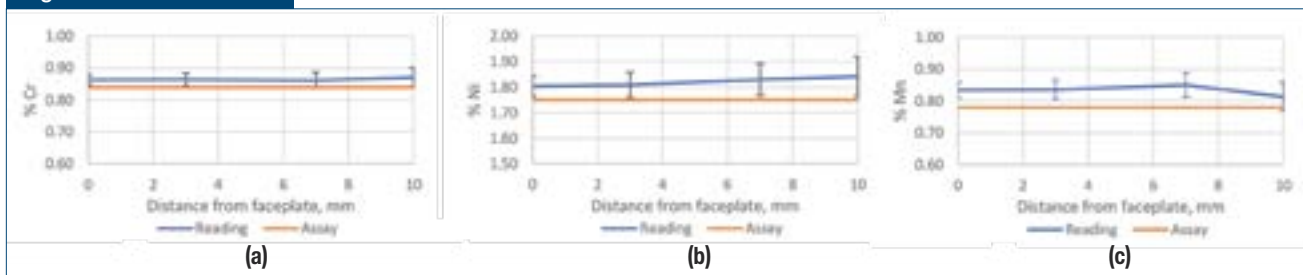
Figure 4
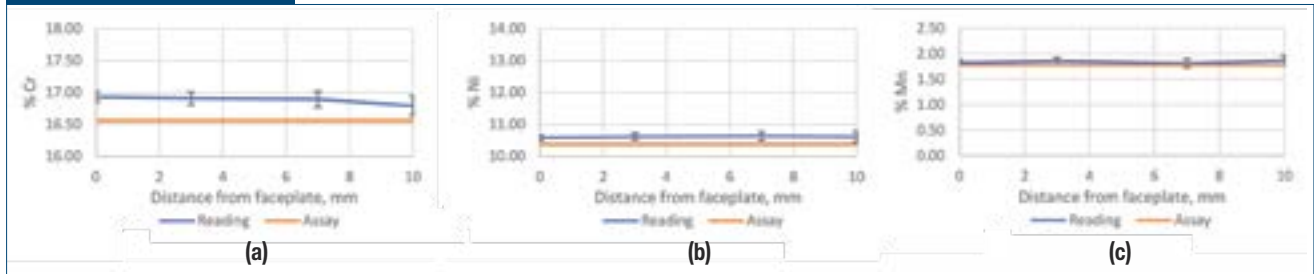
316 stainless steel results, tungsten silicon drift detector (SDD) model: chromium (a), nickel (b) and manganese (c).
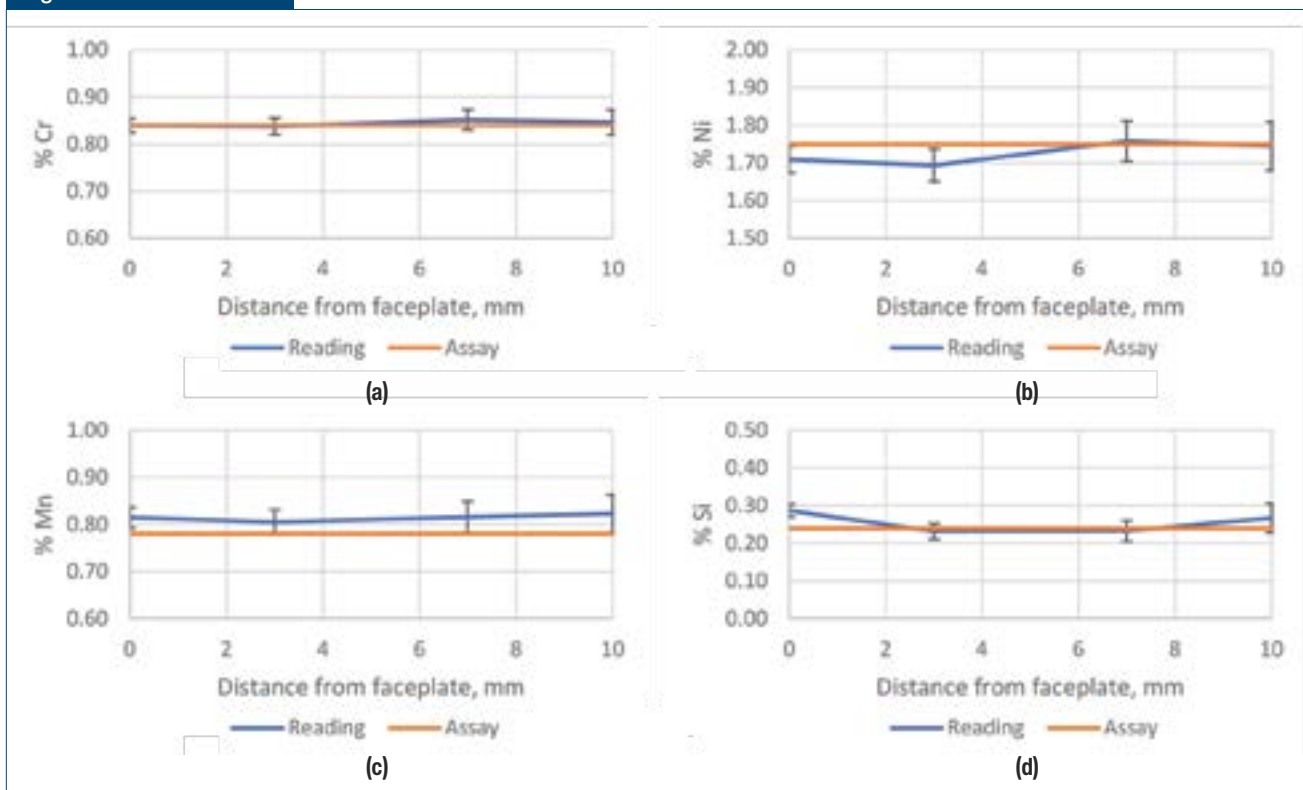
Figure 5
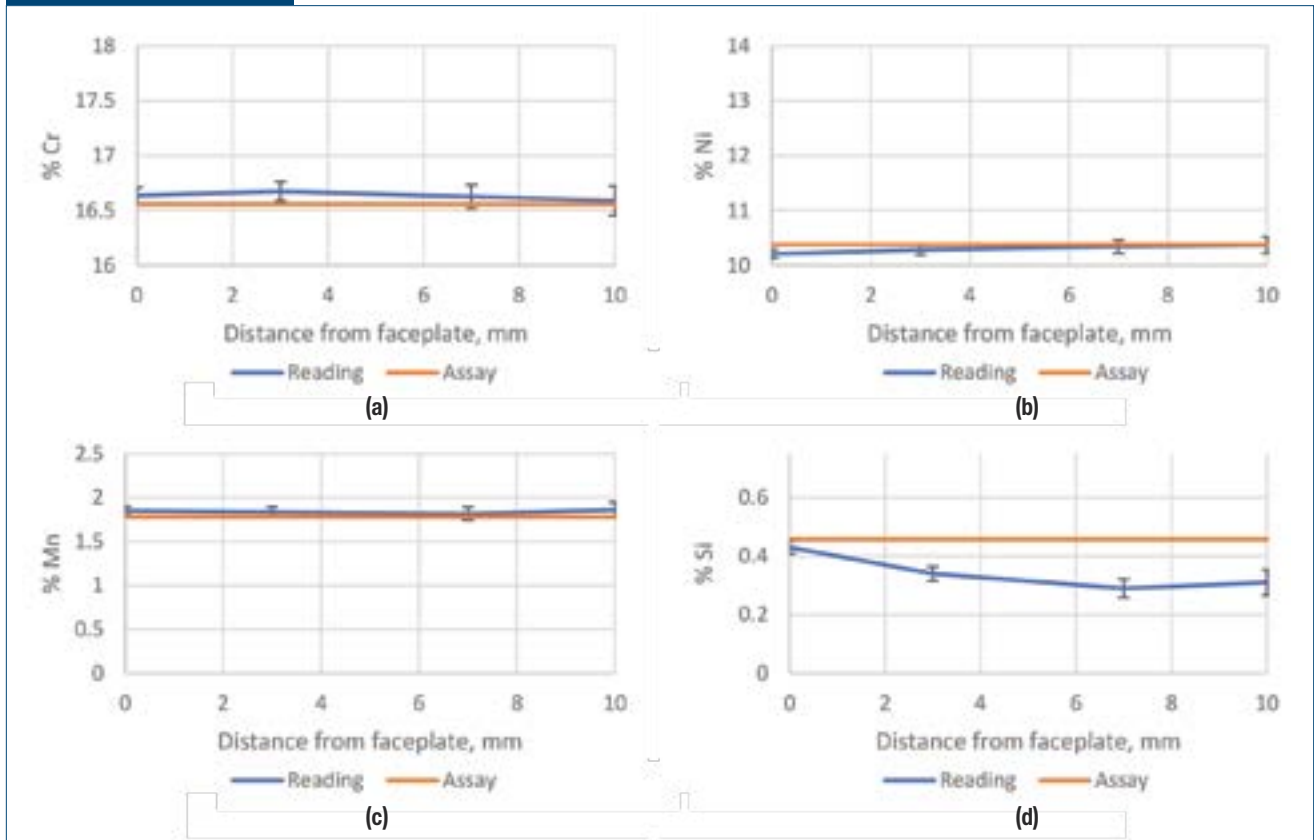
316 stainless steel results, rhodium large SDD model: chromium (a), nickel (b), manganese (c) and silicon (d).

Figure 6

AISI 4340 alloy steel results, tungsten SDD model: chromium (a), nickel (b) and manganese (c).

Figure 7

AISI 4340 alloy steel results, rhodium large SDD model: chromium (a), nickel (b), manganese (c) and silicon (d).

distance causes fewer fluoresced x-rays from the sample than if it were closer to the faceplate. However, users can apply a factor in the instrument software to bring the results back in line with expected assay values. This feature is particularly useful to users who plan to nominally run the sample in excess of 10 mm/1 cm.

Results

Two alloy samples were analyzed: 316 stainless steel (ARMI 5D) and 4340 alloy steel (ARMI 31C) certified reference materials (CRMs) with the fixed distance offsets of 0, 3, 7, and 10 mm. Ten repeat tests were completed. For elements with $Z \geq 22$ (titanium (Ti) and higher on the periodic table), a 40 kV energy beam with an aluminum filter was used to fluoresce the sample. When $Z < 22$ (below Ti on the periodic table) was analyzed, an 8.4 kV energy beam with no filtering was used to fluoresce the sample. Beam times used for analysis were 3 seconds for the 40 kV beam and 5 seconds for the 8.4 kV beam. Relevant common alloying elements[3] were monitored for changes over the varying distance.

316 Stainless Steel Results (UNS S31600), CRM ARMI 5D — Figs. 4 and 5 show the alloying element results for

the varying analysis distances for the 316 stainless steel (ARMI 5D CRM) tested with the tungsten and rhodium models. Each point is the average of the ten repeat tests. Error bars indicate a 1-sigma error for the reading. For the best confidence interval, apply a 3-sigma error. All test results fall within a 3-sigma error to the assay reading.
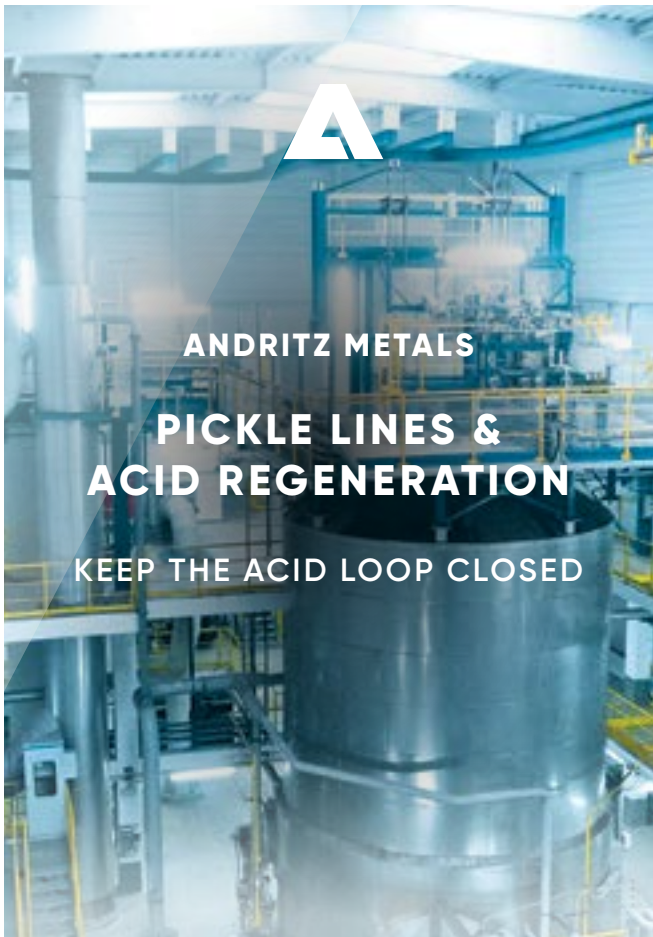
AISI 4340 Alloy Steel Results (UNS G43400), CRM ARMI 31C — Figs. 6 and 7 show the alloying element results at varying analysis distances for the 4340 alloy steel (ARMI 31C CRM) tested with the tungsten and rhodium models. Each point is the average of the 10 repeat tests. Error bars indicate a 1-sigma error for the reading. For the best confidence interval, apply a 3-sigma error. All test results fall within a 3-sigma error to the assay reading.

Conclusions

Both the tungsten and rhodium models maintained accurate performance for materials tested up to a 10-mm distance from the instrument faceplate. Elements of differing fluorescent energy had little effect on accuracy to the assay with varying distances. Varying elemental alloying content had no effect on the accuracy to the assay for either model.

References

1. H.A. van Sprang, "Advances in X-Ray Analysis," *ICDD,* Vol. 42, 2000.
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3. W.L. Phillips, H.H. Hashim and B. Valerioti, "Effect of Residual Copper, Nickel, and Chromium on the Corrosion Resistance of Carbon Steel in Hydrofluoric Acid Alkylation Service," *NACE Corrosion 93 Conference,* paper 623. ✦