

Quick and Correlative TOF-SIMS Analysis of Dispersoid Content in Powder Feedstock and Printed Oxide Dispersion Strengthened Alloys

Laura G. Wilson^{1*}, David L. Ellis², Timothy M. Smith², John T. K. Kim³, and Jennifer. L. W. Carter¹

¹. Materials Science and Engineering Department/Case Western Reserve University, Cleveland, OH, USA

². High Temperature and Smart Alloys Branch/NASA Glenn Research Center, Cleveland, OH, USA

³. Swagelok Center for Surface Analysis of Materials, School of Engineering/Case Western Reserve University, Cleveland, OH, USA

* Corresponding author: laura.g.wilson@case.edu

Oxide dispersion strengthening (ODS) of metal alloys, when combined with additive manufacturing (AM), can be used to solve high-temperature material application problems. It was anticipated that ODS materials, widely studied from the 1960s-80s, were to be the panacea for increasing the operating temperatures or lifetime for nearly any application. However, due to being difficult and expensive to manufacture by conventional approaches, ODS alloys were never widely used [1]. Additive manufacturing provides a way to design and produce complex-shaped metal parts from feedstock powders using Laser Powder Bed Fusion (LPBF) [2].

The performance of ODS materials is dependent on nano-scale oxide being distributed uniformly throughout the metal matrix; a homogenous distribution is critical to the creep and yield strength [3]. Therefore, quantifying and analyzing these oxide nanoparticles is essential for ODS alloy development. Assessing the chemistry and morphology of dispersoids in a material can be conducted using a variety of X-ray and electron-based methods. One of the easiest ways is with qualitative interpretation of grayscale micrographs from Scanning Electron Microscopy (SEM). For quantitative analysis, other methods must be employed, with varying spatial resolution and degrees of difficulty in data collection and sample preparation. Electron-based analysis techniques such as Energy Dispersive Spectroscopy (EDS), Wavelength Dispersive Spectroscopy (WDS), and Electron Backscatter Diffraction (EBSD) require minimally more sample preparation and are quick to collect. The spatial resolution limitation of these techniques arises from the interaction volume of the electron source on the sample which is dependent mainly on the electron beam current and voltage. Fairly high voltages are required to either induce the excitation of a characteristic X-ray from different elements (EDS, WDS) or dynamical diffraction (EBSD), which means that data from much more than $1 \mu\text{m}^3$ is being collected, which is too large to quantitatively identify nanoscale dispersoids. The chemical resolution of these techniques is limited by the degree to which the characteristic signals overlap [4].

One characterization technique that could be successfully employed to analyze the nano-scale oxides is X-ray photoemission spectroscopy (XPS), which collects data from a sufficiently small interaction volume, but there are similar photoelectron energy and Auger peak energy overlaps that can complicate the results interpretation [5, 6]. Transmission Electron Microscopy (TEM) provides the pinnacle of chemical and microstructural resolution, but the small sample size requires lengthy preparation and does not allow for statistically significant analyses. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS), which assesses chemical concentrations from ion masses, provides an alternative for material systems where the characteristic x-ray or electron spectra overlap for different elemental species [7]. The sample preparation and data acquisition are similar to SEM-based techniques, and the interaction

depth between the source and the sample results in chemistry measurements from the top few nanometers of the sample. Therefore, selection of the proper chemical analysis tool is dependent on the necessary spatial resolution and potential spectral overlap of all elements present.

In this work, preparing ODS powder feedstock and LPBF printing was conducted with a NiCoCr alloy and yttria dispersoid. For the AM ODS feedstock powder, it is important that very small oxide powder is mixed with the much larger base metal powder to form a homogeneous oxide coating on the metal powder particles [8]. The AM feedstock powder was prepared by acoustic mixing, with mixing time and force being the two variables of concern. After mixing, the powder was used to print solid samples using an EOS M100 3D printer. For the printing, laser power and scan speed were the two independent variables. TOF-SIMS data were collected on both the powder and printed samples. Imaging of samples was performed using a Tescan Maia3 SEM using a 5 kV accelerating voltage. Chemical analysis was performed on a Physical Electronics NanoTOF TRIFT V TOF-SIMS using a liquid Gallium ion source, at 30 kV and 1 nA. The number of yttrium and cobalt ions emitted from the surface were measured in the static SIMS range using bunched, positive acquisition mode with electron and ion neutralization.

The TOF-SIMS results collected on the feedstock powder samples correspond to the qualitative interpretation of the homogeneity of the oxide coating on the metal powder from SEM images, shown in Figure 1. This provides quantitative support to the qualitative microscopy images collected earlier in the process design phase. The variance in the yttrium distribution on the powder feedstock samples also correlated with the variance of the yttrium distribution detected in the printed samples. This correlation supported the hypothesis that an even coating of yttria on the metal powders contributes to an even distribution of yttria in the printed material.

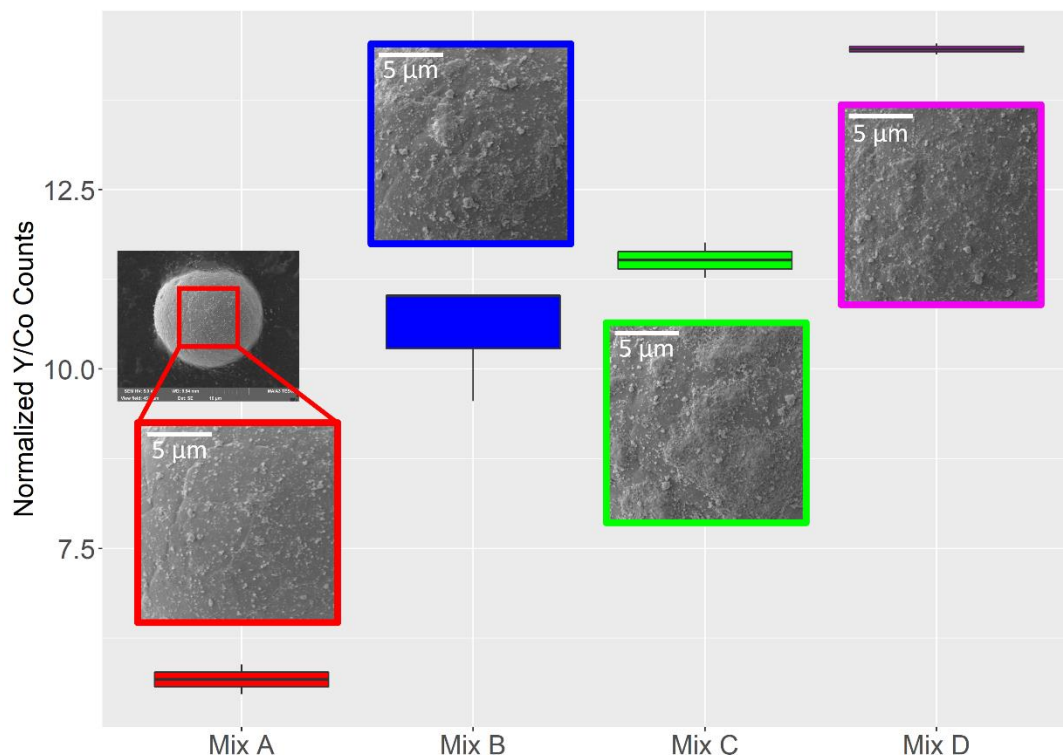


Figure 1. TOF-SIMS data of the yttrium counts relative to the cobalt counts for each mix. Accompanying SEM images show the oxide powder coating on the surface of powder particles.

The spatial distribution of the yttria particles within the printed samples was calculated from the TOF-SIMS data. SEM images of the same printed samples require complicated image analysis to threshold, segment, and accurately measure the spatial distribution of the particles, but the unprocessed micrographs do provide valuable qualitative support to the TOF-SIMS data [9].

References:

- [1] G. M. Ault and H. M. Burte, Proceedings of Metallurgical Society Conference, Vol. 47: Oxide Dispersion Strengthening (1966), p. 3-57.
- [2] J. J. Lewandowski and M. Seifi, Annual Review of Materials Research vol. 46, no. 1 (July 2016), p. 151-186. doi: 10.1146/annurev-matsci-070115-032024.
- [3] G. S. Ansell, Proceedings of Metallurgical Society Conference, Vol. 47: Oxide Dispersion Strengthening (1966), p. 61-141.
- [4] J. A. Bearden, Reviews of Modern Physics vol. 39, no. 1 (January 1967), p 78-124. doi: 10.1103/RevModPhys.39.78.
- [5] "Handbook of Auger Electron Spectroscopy", ed. K. D. Childs et. al., (Physical Electronics, Eden Prairie, MN, 1995).
- [6] "Handbook of X-Ray Photoelectron Spectroscopy", ed. J. F. Moulder et. al., (Physical Electronics, Eden Prairie, MN, 1995).
- [7] "Atomic Weights and Isotopic Compositions for All Elements." https://physics.nist.gov/cgi-bin/Compositions/stand_alone.pl (accessed Jan. 27, 2022).
- [8] T. M. Smith, et. al., Scientific Reports vol. 10 (2020), p. 9663. doi: 10.1038/s41598-020-66436-5
- [9] The work was funded by NASA NSSC grant 18K1737. TOF-SIMS was conducted at the Case School of Engineering, Swagelok Center for Surface Analysis of Materials (SCSAM). Financial assistance for instrument time and scientific training was provided by the SCSAM Fellowship program which is supported by The Swagelok(R) Center for Surface Analysis of Materials Endowment Fund.