Keysight Technologies
Express Test Indentation for High-Resolution Mechanical Mapping of High-Entropy Alloys at High Temperatures

Application Note
Introduction

Useful for high-temperature applications, newly developed high-entropy alloys (HEA) exhibit superior mechanical properties at high temperature when compared with conventional superalloys or structural ceramics [1]. The term high-entropy is associated with the stable solid-solution formation phase resulting from high configurational entropy [2]. However, presence of multi-phase microstructures in some HEA compositions indicate that factors such as mixing enthalpy and hence solubility of elements may also be predominant when controlling segregations during solidification, therefore promoting multi-phase structures. Due to the equimolar presence of several elements in the alloying system, mechanical properties at high temperature are influenced by the diffusion rate of each element in multi-phase systems.

With the help of high-temperature nanoindentation technology, probing variations and diffusion effects of HEAs’ mechanical properties at the nano-scale is possible. Express test (ET), used with Keysight’s G200 nanoindentation system, enables monitoring of local mechanical property changes from room temperature (25 °C) up to 500 °C. Fast indentation integrated with a high-temperature laser heater system provides accurate, local measurements of mechanical variations in the microstructures. By controlling the load or indentation depth, it is possible to create large indentation arrays to map Young’s modulus and hardness within areas of interest to generate high-resolution variation maps of different microstructural features such as different phases, orientations, and grain boundaries. In this application note, we illustrate the mechanical properties of a single-phase CoCrFeNi and dual-phase AlCrFeNiTi with faced centered cubic (FCC) and based centered cubic (BCC) structures at room and high temperatures.

Test Methodology

Samples of CoCrFeNi and AlCrFeNiTi HEA alloys were cut and their surfaces were processed for high-temperature nanoindentation tests. Both alloys with nominal compositions were cast at the University of Science and Technology Beijing (USTB) in China using magnetic levitation equipment, and then cut to 10 mm x 10 mm pieces with a 3-mm thickness. The surfaces of the samples were grinded and polished to roughly 50 nm to achieve a shiny, scratch-free surface. The processed samples were then mounted on a laser heater sample tray for nanoindentation tests. The sapphire laser heater tip capable of being independently heated to testing temperatures similar to the samples was installed on XP indenter head to assure maximum thermal stability. Both the tip and sample temperatures were monitored during the test using the integrated thermocouples with temperature controller software. Figure 1 shows Keysight’s G200 laser heater system and a schematic of the high-temperature nanoindentation set up.
The Express Test (ET) mapping option was used for the nanomechanical measurements. ET was also used in this study to statistically measure the near-surface mechanical properties as well as their variation and distribution at different test temperatures. 100 indents were performed with a 100 µm x 100 µm array for each temperature. The indentation depth was controlled by using the load or displacement control options in ET. The high-resolution mechanical property maps were generated in 200 µm x 200 µm areas on both samples with indentation spacing as small as 2.5 µm. In this configuration, 6400 indents were performed. Different phases or features such as grain boundaries were mapped in addition to the distribution of mechanical properties within the grains. Site-specific nanoindentations using a standard, basic method was also performed on AlCrFeNiTi multi-phase alloys to extract and compare the mechanical properties of individual phases to the statistical findings. Test temperatures for both HEA alloys were set at room temperature (RT), 100 °C, 200 °C, 300 °C, 400 °C and 500 °C. Argon gas was purged during the test to avoid any contamination and oxidation at elevated temperatures. More details on the setup are provided in other Keysight application notes referenced in notes [3-6].

Measurement Results

High-temperature statistical nanoindentation on single-phase alloy

A load-control ET method with a predefined load of 15 mN was used to perform high-speed indentation on the single-phase CoCrFeNi alloy. Figure 2 shows the modulus and hardness results of the alloy at a temperature range from 25 °C to 500 °C. There is a variation in the modulus and hardness of material from point to point, reflecting the differences in the grain orientation or grain boundaries of the microstructure. As the temperature increased, these variations became more significant, particularly around 400 °C for Young’s modulus of the material, which reflects the elastic properties related to the crystal/phase structures, and orientation dependence. This variation shows some predominant textures growing at certain temperatures or changes in compositional homogeneity in the microstructure which resulted in such variations. Less variation appeared in hardness values, though abnormal behavior was observed at around 400 °C.
Figure 3 lists the average quantified values obtained from ET measurements provided in Figure 1 along with their standard deviations. The indentation depth varied from ~400 nm to 500 nm at different test temperatures for the same applied load. In the application note, Using High-Temperature Nanoindentation to Study Mechanical Properties of High-Entropy Alloys, we provided CSM data on the same material [6]. The results predicted in this ET study have higher values. This is due to the small indentation load applied in this test that resulted in a smaller, more orientation sensitive or phase sensitive indentation depth. It must be noted that these values are also influenced by the size effect at such small indentation depths, which are more significant for higher temperature indentations, as shown in the CSM application note [6]. As the indenter goes deeper into the bulk of the material, the deformation volume of material becomes more reflective of the whole bulk rather than the local properties as all effects are evened out and the properties become constant. Therefore, ET is a powerful method to measure the properties of individual features or phases of the microstructures, as well as a very useful method for composite materials. However, indentation depths beyond the tip edge radius need to be chosen carefully.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Depth (nm)</th>
<th>STD</th>
<th>Modulus (GPa)</th>
<th>STD</th>
<th>Hardness (GPa)</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>407.1027</td>
<td>11.47</td>
<td>255.39</td>
<td>20.17</td>
<td>3.95</td>
<td>0.23</td>
</tr>
<tr>
<td>100</td>
<td>429.357</td>
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<td>254.96</td>
<td>30.13</td>
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<td>0.21</td>
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<tr>
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<td>258.53</td>
<td>39.51</td>
<td>3.17</td>
<td>0.19</td>
</tr>
<tr>
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<td>471.1124</td>
<td>10.58</td>
<td>273.24</td>
<td>33.75</td>
<td>2.87</td>
<td>0.13</td>
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<tr>
<td>400</td>
<td>461.1066</td>
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<td>73.01</td>
<td>3.12</td>
<td>0.18</td>
</tr>
<tr>
<td>500</td>
<td>510.5304</td>
<td>25.66</td>
<td>202.46</td>
<td>39.34</td>
<td>2.50</td>
<td>0.25</td>
</tr>
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</table>

Figure 3. Quantitative modulus and hardness values of a CoCrFeNi single-phase HEA alloy at different temperatures using the ET method.
High-temperature statistical nanoindentation on multi-phase alloy

AlCrFeNiTi has multi-phase BCC structures. The microstructure of this alloy consists of as-cast large dendrites (grains) containing an abundant number of spherical phases that are uniformly distributed with an average size of 1 µm, surrounded by the eutectic phase. The eutectic phase also consists of needle-like morphology precipitates with widths that vary from 1 to 5 µm. Figure 4 shows the optical image of an AlCrFeNiTi microstructure and the abovementioned phases. According to a previous study held at USTB using scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX), the matrix of the dendritic structure (A) is rich in Cr and Fe, but the surrounding eutectic phase (B) is rich in Al, Ni and Ti [7]. Spherical small precipitates within the dendrites are rich mainly in Al and Ni [7]. Transmission electron microscopy (TEM) studies indicated that spherical small phases have ordered BCC structures, while needle-like precipices in the eutectic phase contain the same main elements (Al and Ni) but with disordered BCC structures [7].
Basic, standard indentation tests were performed selectively on individual phases with a small indentation depth (300 nm) to estimate the properties of each phase. A basic test was performed on the needle-like phase, in the matrix of grains where there are no spherical precipitates, and in the matrix of eutectic where there is no needle-like phase. According to these measurements, the modulus and hardness of the grain matrix is 255 GPa and 7.5 GPa respectively. For the eutectic matrix, the values are 213 GPa and 7.66 GPa respectively, and for the needle-like phase, they are 209 GPa and 8.30 GPa, respectively. Spherical phases are too small for selective nanoindentation tests. To extract the properties of this phase, ET was performed inside the grains within the areas that contain only dendritic structures. Figure 5 shows the hardness and modulus variations after data analysis. In our ET test, the load was chosen to achieve an indentation depth in the range of 250-300 nm, comparable to the basic test.

Clearly, the histograms do not reflect the unimodal or normal distributions, as expected. Distributions are somewhat skewed, not centered around the mean of the values. The Young’s modulus histogram has two main peaks that are far away from each other: one around 237 GPa and the other around 251 GPa. Basic tests of the grain’s matrix showed the modulus around 255 GPa which perfectly matches one of these peaks. We assume that the other one corresponds to the other phase, which are spherical precipitates. From the hardness histogram, it is hard to find clear peaks separated from each other. Since the hardness responds to the deformation volume underneath the indenter and in the composite structures, particularly those with small, hard precipitates in the soft matrix, the response of deformation volume cannot be directly related to the individual phases’ behavior. However, from the hardness histogram we see two major distinguishable values: one around 7.7 GPa and the other around 8.3 GPa, which may correspond to the matrix and precipitates respectively.

Figure 5. Histograms of modulus and hardness variation of an AlCrFeNiTi multi-phase alloy in the grains measured using the ET method.
Figure 6 shows some of the results from a high-temperature ET study on a multi-phase alloy. Since the data corresponds to the various phases, we expect to see multi-modal behavior in both modulus and hardness of material. The median of data is not being used to report the overall properties at different temperatures, as the graphs do not follow normal distribution patterns. As shown in the table below, the median of modulus is increases up to 400 °C and then suddenly decreases at 500 °C in Young’s modulus of material. Again, a load was selected to examine the elastic/plastic response at a shallow, 300 nm depth so that properties of individual phases could be detected. Hardness measurements show a gradual decrease as temperature increased related to the plastic deformation and softening behavior of material at higher temperatures. The distribution of modulus and hardness for temperatures between 200 °C and 500 °C are also shown in Figure 6. In modulus histograms, the distribution of the data changes from multi- or bi-modal to almost normal behavior. This might be due to the high diffusion rate of elements which dramatically changes above 500 °C as reflected in the modulus data. However, understanding such behavior needs further compositional and microstructural analysis.

<table>
<thead>
<tr>
<th>Temperature (° C)</th>
<th>Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>224</td>
<td>5.8</td>
</tr>
<tr>
<td>200</td>
<td>227</td>
<td>5.7</td>
</tr>
<tr>
<td>300</td>
<td>235</td>
<td>4.6</td>
</tr>
<tr>
<td>400</td>
<td>250</td>
<td>4.3</td>
</tr>
<tr>
<td>500</td>
<td>200</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Figure 6. Median of modulus and hardness of an AlCrFeNiTi multi-phase alloy at different temperatures. Histograms of modulus and hardness are measured using the ET method.
High-resolution nanomechanical properties mapping

Figure 7 illustrates the modulus and hardness mapping of both single-phase and multi-phase alloys. Instead of choosing different locations to collect the statistical data, a nanoindentation test was performed within a specific area by controlling the indentation depth and spacing, to generate high-resolution maps. Although a single-phase alloy consists of only one phase, there is a variation in the Young’s modulus of material throughout the microstructure. These maps are generated at room temperature on annealed microstructures after rapid cooling down from 500 °C.

The distribution of the modulus in maps for both materials perfectly match the microstructures shown in the Figure 7. Young’s modulus is dependent on both the structure and orientation of the phases. The modulus study is a better reflection of the microstructure than the hardness study, which is more reflective of the plastic deformation underneath the indenter. Clearly, different crystallographic orientations as well as grain boundaries show different elastic properties in response to the nanoindentation.

Figure 7. Mapping of high-resolution mechanical properties of multi-phase HEA alloys at room temperature after rapid cooling down from 500 °C.
Figure 8 shows the quantified modulus and hardness distributions corresponding to the mapping measurements shown in Figure 7. The graphs correspond to a very large data set of 6400 indents per graph. They mostly follow a normal distribution. However, for multi-phase alloy, there are two detectable peaks in Young’s modulus graph related to the two different phases in the microstructure.

![Graphs of modulus and hardness distributions](image)

**Figure 8.** Modulus and hardness distributions from high-resolution mechanical properties mapping for single- and multi-phase HEA alloys at room temperature after rapid cooling down from 500 °C.

**Conclusions**

The Express Test (ET) method used in this study is a very powerful and fast method to statistically evaluate the properties of HEA single-phase and multi-phase alloys. Extracting the properties of individual phases is possible by collecting a large data set of indents all over the microstructure. This method was also modified to dynamically measure the mechanical properties of materials at high temperatures using the Keysight’s G200 laser heater system. Using this method, high-resolution mechanical property maps can be generated, which enables scientists to study detailed mechanical property variations in materials with a one-to-one comparison with microstructural and compositional variations. It can also be used to make comparisons with the mathematical and mechanical modeling results.
Acknowledgment

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References


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