LEAP MICROSCOPES LOOK AT TiAl ALLOYS

The Local-Electron Atom-Probe (LEAP) microscope helps to investigate how nanoscale precipitates strengthen TiAl alloys at elevated temperatures and stresses in proposed jet engine and aerospace applications.

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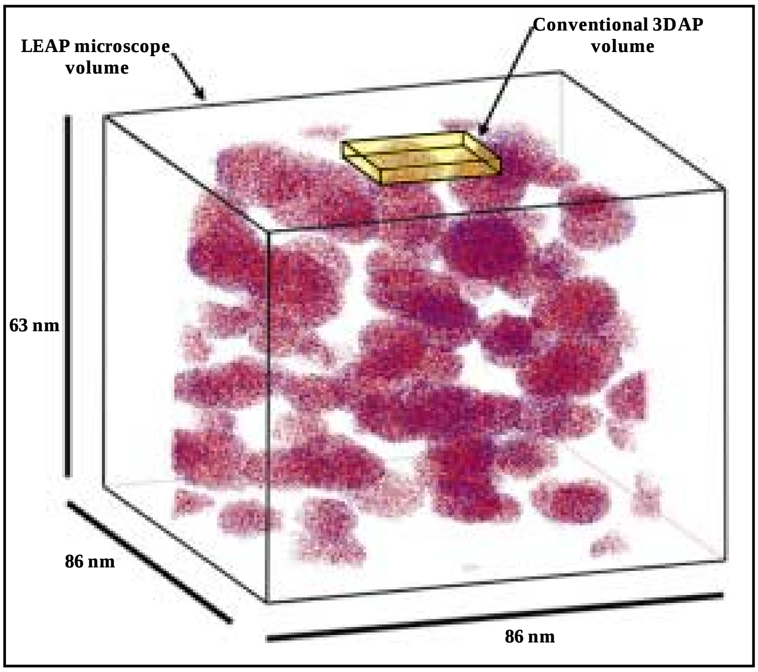

Fig. 1 — Analysis volume collected on a specimen of a nickel-aluminum-chromium alloy in approximately one hour using the LEAP microscope, versus the volume that would be collected in the same amount of time on a conventional 3DAP (highlighted in yellow). Only Al (red) and Cr (blue) atoms within gamma-prime precipitates are shown for clarity. This image is courtesy of Chantal K. Sudbrack of Northwestern University.

The local-electrode atom-probe (LEAP) microscope is a variation of the three-dimensional atom probe (3DAP) microscope, in which pulsed electric-field or laser-beam pulsed evaporation reveal the nanostructure of materials on an atom-by-atom basis. 3DAP microscope analysis locates and identifies specific isotopes and their locations in a specimen. The 3DAP microscope stands alone in its ability to combine structural and compositional information at the atomic level, and thus it provides investigators with a truly unique three-dimensional and atomic-scale view of materials.

The 3DAP microscope determines the chemical identities of analyzed atoms by time-of-flight mass spectrometry, and as a result light elements such as carbon or oxygen are detected with the same efficiency as heavier elements. Thus, the concentrations of light elements, which potentially play an important role in precipitate nucleation and growth, are readily measured by 3DAP microscopy.

However, the 3DAP microscope is not widely used because of its slow analysis speed and small analysis volumes. For example, a typical data set acquired by a conventional 3DAP microscope represents an analysis volume of only approximately 15 x 15 x 100 nm and requires two days to collect. Particularly for studies of precipitates, a small analysis volume means that multiple analyses may be required to capture a single precipitate within the analyzed volume, and acquiring statistically significant information about precipitates becomes a very time-consuming process.

However, the LEAP microscope can achieve analysis rates that are at least 600 times faster and analysis volumes at least 100 times larger than conventional 3DAP microscopes. Figure 1 shows the corresponding difference in analysis volume collected during a one-hour assay on a conventional 3DAP microscope versus the LEAP microscope for a nickel-aluminum-chromium alloy.

The synergy between faster analysis and larger analysis volume means that the LEAP microscope can detect statistically significant numbers of precipitates in a single analysis in a relatively short time. Detecting large numbers of precipitates (tens to hundreds or thousands depending on their number density) provides higher quality information about precipitate morphology and improves accuracy of compositional data.

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This article describes how the LEAP microscope provides unique information that may be exploited for optimizing TiAl alloy compositions.

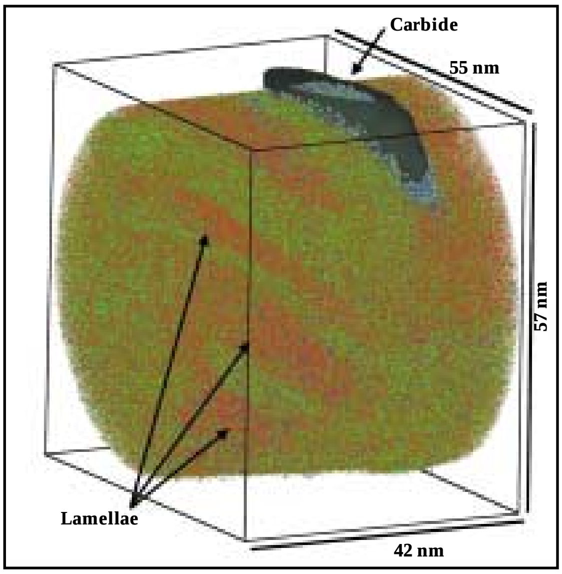

Fig. 2 — Three-dimensional atom-map obtained from a LEAP microscope analysis of a model TiAl alloy with carbide precipitates. Image displays Al atoms (red), Ti atoms (green), C atoms (grey), and O atoms (blue), with a 4.5 at.% C isoconcentration surface revealing an oxycarbide precipitate among the lamellae. The reconstruction represents a volume of 57 x 55 x 42 nm and contains 3.6 million atoms.

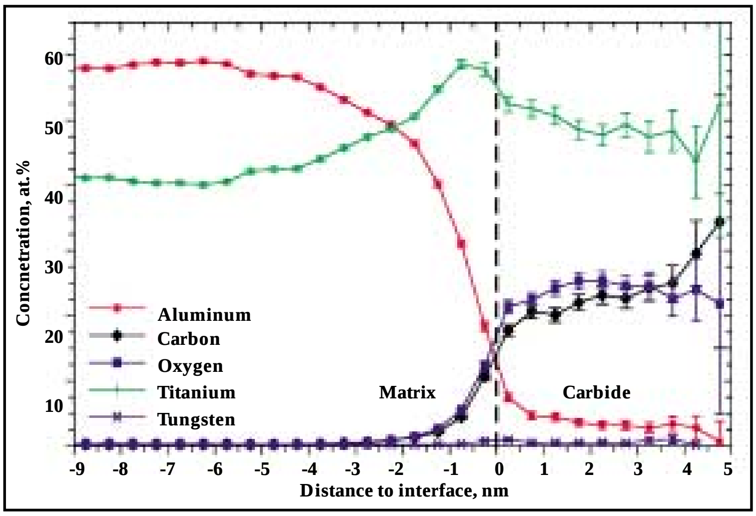

Fig. 3 — Proximity histogram of the analyzed volume shown in Figure 4 displaying concentrations with respect to a carbon isoconcentration surface (4.5 at.% C). Carbide concentration is on the right-hand side, matrix concentration is on the left-hand side of the figure. The proxigram highlights the very high oxygen concentration within the carbide.

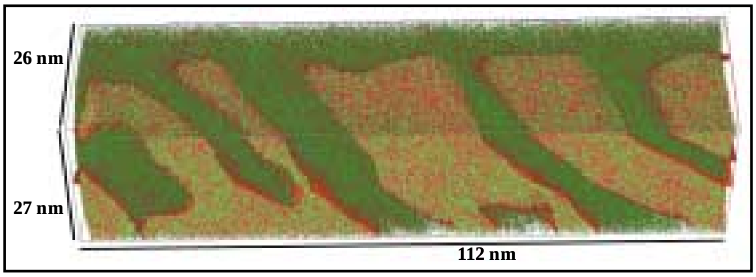

Fig. 4 — Ultrafine lamellar microstructure as determined by applying an atom map from a LEAP microscope analysis. Aluminum and titanium atoms are represented by red and green dots, respectively. The volume shown is approximately 26 x 27 x 112 nm and consists of information from 2.3 million atoms.

It presents results of a research study on the size scale of strengthening lamellae and the chemistry of carbide precipitates in TiAl alloys.

Nanoscale clues in TiAl

In the case of the TiAl alloys, in which the number density of strengthening precipitates is lower than that of the material shown in Fig. 1, the larger analysis volume provided by the LEAP microscope is even more important because it greatly increases the chances of capturing at least one precipitate per specimen analysis.

The research presented here considers the role of oxygen in the formation of nanoscale features. Oxygen is an unavoidable impurity that is incorporated in TiAl alloys during processing. It has been argued that the oxygen concentration may influence microstructural kinetics in TiAl alloys. To investigate the potential correlation between oxygen and precipitate formation and growth, the LEAP microscope was used to measure oxygen concentrations in carbide precipitates and the surrounding matrix.

The material selected for the study was a TiAl alloy with the nominal composition $Ti_{48}Al_{51}W_{0.5}C_{0.5}$,

Designing better TiAl alloys

High-temperature creep strength emerges as a key limiting factor to the widespread use of TiAl alloys. Two microstructural features that improve creep resistance are lamellar microstructure and precipitates at the lamellar interfaces.

Lamellar thickness has been shown to influence the creep behavior of gamma TiAl with progressively smaller spacings (down to 10 nm) corresponding to higher creep resistance. Figure 4 shows an example of an ultrafine lamellar structure in the form of an atom-by-atom three-dimensional reconstruction. Aluminum atoms are displayed in red and Ti atoms in green. Figure 5 displays the same structure with isoconcentration surfaces corresponding to 51 at.% Al and reveals an average lamellar thickness of 9 nm.

Titanium aluminide (TiAl) alloys have the potential to meet today's drive for more efficient engines. Approximately half as dense as nickel-based superalloys, titanium aluminide alloys demonstrate good oxidation and room temperature creep resistance and high strength. They also have valuable properties for high-temperature structural applications, including exceptionally good high-temperature strength, oxidation resistance, and hot-corrosion resistance. These properties combined with light weight translate into greater fuel efficiency.

A primary limitation to more widespread use of TiAl alloys is their high-temperature creep resistance. Fine scale lamellae (10 to 30 nm thick) of the tetragonal gamma TiAl and hexagonal alpha-2 Ti_3Al phases in combination with ceramic-type precipitates have been shown to increase significantly the creep strength of TiAl alloys.

Ceramic precipitates, some of which form preferentially within the gamma-TiAl phase (i.e., perovskite structured Ti_3AlC carbides) and others at heterophase interfaces (i.e., hexagonally structured Ti_2AlC carbides and Ti_5Si_3 silicides), also increase creep resistance at elevated temperatures. Understanding how precipitates nucleate, grow and coarsen will assist materials engineers in the design of alloys with acceptable creep resistance above 800°C (1470°F).

in which carbon combines with titanium, aluminum, or oxygen to form strengthening precipitates. Tungsten provides additional solid-solution creep strengthening. The TiAl was annealed at 1250°C (2280°F), followed by quenching and aging at 800°C (1470°F) for 24 hours, to capture the initial stages of carbide growth.

A three-dimensional reconstruction from a LEAP microscope analysis of a specimen of the alloy is displayed in Fig. 2. This figure shows a subset of data containing 3.6 million atoms in a volume that is approximately 57 x 55 x 42 nm. The complete data set contains approximately 13.5 million atoms, which was recorded in 0.5 hours. Fine lamellar structures and a portion of a carbide precipitate are clearly reconstructed. The lamellae range in thickness from 3.1 to 8.3 nm, and the carbide precipitate measures approximately 5 nm in diameter.

In addition to the qualitative atomic map presented in Fig. 2, LEAP microscope data can be analyzed quantitatively. A recently developed quantitative analysis technique called the proximity histogram (or proxigram) displays chemical concentrations with respect to a defined interface within a nanostructure. The interface is defined by specifying the concentration of an element, which leads to an isoconcentration surface. The topology of this interface can be either locally convex or concave. Therefore, this analysis approach permits information from a three-dimensional space to be displayed in a two-dimensional concentration profile independent of the morphology of the precipitate.

Oxygen concentration

The proxigram approach on data acquired by a LEAP microscope demonstrates that the oxygen concentration within the carbide precipitate is similar to that of carbon (Fig. 3), such that its stoichiometry is $Ti_{48}Al_4W_1C_{23}O_{24}$. This composition implies that the precipitates are of the TiC type, but with a significant oxygen concentration. Thus this precipitate is appropriately labeled a Ti(C,O) oxycarbide. Oxycarbides have also been found to exist for the perovskite Ti_3AlC and hexagonal Ti_2AlC type carbides; oxygen concentrations were measured to be between 8 and 14 at. %, revealing $Ti_3(Al,C,O)$ and $Ti_2Al(C,O)$ oxycarbides, respectively.

These findings are consistent with other research that shows that oxygen partitions strongly to ceramic-type strengthening precipitates. Thus, in designing new alloys, the oxygen concentrations should be considered in addition to the metallic elements, as oxygen may ultimately determine the stability of nanoscale strengthening precipitates in TiAl-based alloys.

High-temperature creep resistance properties of TiAl and other alloys originate from microstructural features that occur at the nanoscale, such as ultrafine lamellar spacing and nanometer-size precipitates. Thus, it is increasingly important to study alloys such as TiAl on correspondingly finer length scales. Atomic-scale characterization with the LEAP microscope provides insights into nanoscale features that strengthen TiAl alloys, and builds the foundation for the increased use of these alloys in automotive and aerospace applications. ■

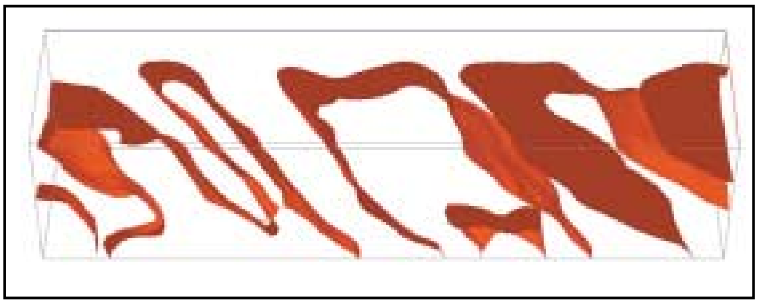

Fig. 5 — Isoconcentration surface corresponding to 51 at.% aluminum delineates fine scale lamellae with thickness ranging from 4 to 24 nm in a TiAl alloy.

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