Properties and influence of crystal defects in Fe$_2$VAl synthesized by laser surface remelting

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Abstract

Laser surface remelting can be used to manipulate the microstructure of cast material. Here, we present a detailed analysis of the microstructure of Fe$_2$VAl following laser surface remelting. Within the melt pool, elongated grains grow nearly epitaxially from the heat-affected zone. These grains are separated by low-angle grain boundaries with $1^\circ$–$2^\circ$ misorientations. Segregation of V, C, N at grain boundaries and dislocations is observed using atom probe tomography. The local electrical resistivity was measured by an in-situ four-point-probe technique. A smaller increase in electrical resistivity is observed at these low-angle grain boundaries compared to high-angle grain boundaries in a cast sample. This lays the foundation for manipulating thermoelectric properties through grain boundary engineering.

Keywords

Thermoelectric materials, atom probe tomography, microstructure, grain boundary defects, laser surface remelting
Environmentally-friendly power generation is a major societal challenge currently faced by scientists. Research interest in thermoelectric (TE) materials is hence on the rise (again). Thermoelectricity is caused by the Seebeck effect [1]. While the physical background is well laid out, several strategies to increase efficiency have remained unexplored. The high price or the toxicity of the elements constituting the materials have hindered widespread applications. Hence, a non-toxic and cost-effective alternative is needed.

A promising candidate is the full Heusler compound Fe$_2$VAl. The power factor of Fe$_2$VAl is high (>5 mW m$^{-1}$ K$^{-2}$ at 300 K) [2] and can compete with state-of-the-art materials such as Bi$_2$Te$_3$ [3,4]. Yet, the high thermal conductivity $\kappa$ restricts its thermoelectric performance. Therefore, the main aim is to increase phonon scattering to reduce $\kappa$. Possible approaches are doping [5–7], off-stoichiometric compositions [8–11], introduction of defects and disorder [12–14], and interfaces [15,16]. The microstructure can be manipulated by adjusting the synthesis route. A powerful way to change and control the microstructure is laser surface remelting (LSR) [17]. A focused laser beam is scanned over the surface, leading to a fast melting and subsequent solidification. The laser power and the scan velocity can be changed to adjust the peak temperature, the solidification speed, and, thus, the resulting microstructure. LSR ensures a high quenching rate on the order of $10^3$-10$^8$ K/s [18], which depends on the scanning parameters. The parameters used here are expected to lead to an approximate quenching rate of $10^4$-10$^5$ K/s.

Here, we focus on the microstructure of Fe$_2$VAl following LSR and its local influence on the electrical resistivity. Emphasis is placed on dislocations and low-angle grain boundaries (LAGB), and associated solute segregation.

Local measurements of the electrical resistivity show that LAGBs do not significantly affect the electrical resistivity compared to high-angle GB (HAGB) in the Fe$_2$VAl system. Our study advances the understanding of the microstructure – property relationship in these alloys, offering opportunities for further optimization of the thermoelectric performance.

Stoichiometric amounts of pure Fe (99.9%, Carboleg GmbH), Al (99.7%, Aluminium Norf), and V (99.9%, HMW Hauner GmbH) were arc-melted under an argon atmosphere. To ensure homogeneity, the sample was flipped over and remelted four times. The chemical composition obtained from inductively-coupled plasma optical emission spectrometry (ICP-OES) is Fe$_{50.09}$V$_{24.95}$Al$_{24.96}$ (at.%). Small amounts of C and N, 0.03 at.% and 0.01 at.% respectively, were found in the bulk by infrared absorption measurement and melting under helium with a subsequent thermal conductivity measurement, respectively.

Before LSR, this arc-melted sample was hand-ground to 600 grit SiC paper to ensure a uniform surface. An AconityMini system by Aconity3D, equipped with an ytterbium-fiber laser with a wavelength of 1070 nm, was used to remelt the surface of the material. The focal size of the laser beam was 90 µm, the laser power $p$ was 200 W, the scanning speed $v$ was 350 mm/s, and the hatch distance $h$ was 0.1 mm. These parameters lead to an energy density $E = \frac{p}{vh}$ of 6.67 J/mm². The melting process was conducted in argon atmosphere with an oxygen concentration below 80 ppm.

Microstructural analysis on the micrometer scale was performed using scanning electron microscopy (SEM) in backscattered electron mode (BSE). The cross-section of the melt pools was mechanically polished down to 0.05 µm
colloidal silica. Imaging, electron backscattered diffraction (EBSD), and energy-dispersive X-ray spectroscopy (EDX) were conducted using a Zeiss 1540 XB SEM. EBSD was performed with a step size of 200 nm and an acceleration voltage of 15 kV. Needle-shaped specimens for atom probe tomography (APT) were prepared using a dual-beam focused-ion-beam (FIB) instrument (FEI Helios Nanolab 600/600i) with a Ga ion source by an in-situ lift-out method and a subsequent sharpening process, as described in Ref. [19]. APT specimens were analyzed using a LEAP™ 5000 XS instrument ( Cameca Instruments) operated in laser pulsing mode using a pulse repetition rate of 200 kHz and a pulse energy of 40 pJ. The base temperature of the specimen was kept at 60 K and the target detection rate was set to 4%. The IVAS 3.8.4 and Matlab R2019 was used for data reconstruction and analysis.

The influence of LAGBs on electronic transport was studied by local electrical resistivity measurements carried-out in-situ inside an SEM (Zeiss Gemini) with a linear 4-point-probe technique. The sample was inserted into an SEM on a stage with 4 independent micromanipulators (PS4, Kleindiek Nanotechnik GmbH). Each micromanipulator contains a needle with a tip radius of approx. 50 nm. The needles are positioned 5 µm apart inside a single grain and then on either side of a GB. The contribution of an individual GB to the resistivity is the ratio between bi- and single-crystal regions. Technical details on the electrical measurements, e.g. errors, corrections due to deviation from equidistance positions of needles and modulation of electrical current, are detailed in Ref. [20].

Fig 1. shows optical and BSE images of the remelted area, in the top view and the cross-sectional view, respectively. Cracks are observed in the optical and low magnification SEM image (Fig. 1a/b). These cracks mainly appear at (high-angle) grain boundaries of the arc melted sample (Supplemental Fig. S1). Similar cracking behavior was observed in superalloys [21,22]. The melt pools are approximately 106 µm deep, 160 µm wide, and show an overlap of two adjacent melt pools of 30 µm. The high magnification BSE image shown in Fig. 1c reveals a structure with elongated solidification cells originating from within the melt pool, surrounded by a heat-affected zone. These cells are akin to individual grains that have grown (nearly) epitaxially, hence sharing nearly the same orientation. These cells, referred to as grains here, are separated by low-angle (grain) boundaries (LAGBs), as discussed later. This small misorientation between the grains leads to a notable contrast in the BSE image. The mean grain size of the elongated grains measured in the center of the melt pool 5 µm away from the surface is approximately 1 µm x 10 µm. Some grains span the entire melt pool from the heat-affected zone to the surface. The average grain size decreases towards the center and the top of the remelted track due to the increased solidification rate. No precipitates can be observed at this scale.

EDX maps show a homogeneous distribution across the melt pool and surroundings (Supplementary Fig. S2). This indicates a homogenous melting and solidification process. No preferential evaporation of an element occurred during melting. No microsegregation at the length scale of the grains can be observed. EBSD was performed to investigate the crystallographic orientation differences within the melt pool (Fig. 2). At room temperature, Fe2VAl crystallizes in the L21 full Heusler phase [23]. With EBSD, all points could be indexed to this phase and no second phase was observed.
The inverse pole figure with [001] reference axis (Fig. 2a) shows little orientation differences within the grain structure. The unremelted grain has approximately a [122] orientation, from which the grains within the melt pool grow nearly epitaxially. The different grains are oriented between [112] and [122] orientation. The misorientation between the second nearest neighbor is displayed in the Kernel map (Fig 2b). The fraction of grain boundaries with different misorientations was calculated and is plotted in Fig. S3 (Suppl. Information). Nearly 50% of all observed boundaries show misorientations of 1° ± 0.25°. The fraction of boundaries with higher misorientations decreases towards a misorientation angle of 10°. These higher misorientations, around 10°, are observed close to the incidence position of the laser at the surface.

The local chemical composition and crystalline defects can alter the TE properties. Therefore, to understand the microstructure-properties relationship, it is important to study segregation phenomena in detail. We used APT to provide insights into the near-atomic distribution of the elements, in search for possible segregation or clustering within the melt pool. APT specimens from a region close to the surface of the melt pool are investigated. The region for the lift-out is marked in Fig. 1b) by the blue box (not to scale). Fig. 3a) shows a representative APT reconstruction. The Fe, V, and Al ions are visualized as blue, green, and orange dots, respectively. The black iso-composition surface indicates regions with a composition above 0.5 at.% VN, VC, N, and C ions combined. A boundary and several dislocations are observed, covered with VCₙNₓ precipitates. The dislocations are observed near the boundary and in the bulk. The dislocation density is moderate with an approximate distance of less than 100 nm between dislocations.
To investigate the type of boundary, three APT detector hit maps on either side and at the boundary were plotted (Fig. 3b). The position of the (111) pole is observed in each map. The (011) pole is also clearly visible but due to its larger size, the central position is more difficult to determine. Two more {011} poles are slightly outside the desorption map. The second map shows a darker feature, indicated by the black arrows. This feature corresponds to the grain boundary. The distance on the detector between the pole on either side of the boundary is 1.4 mm, which corresponds to a misorientation of the LAGB of approximately 1.1° assuming that the field-of-view is close to 60° on this instrument [24]. Thus, the observed boundary is a LAGB with a misorientation similar to the typical misorientation determined by EBSD measurements.

A composition profile was calculated along a cuboidal region-of-interest (5x13 nm²) with a step size of 0.4 nm (Fig. 3c) across the LAGB. The position of the profile is indicated by the black arrow in Fig. 3a. This compositional plot is exemplary for the compositional changes across the boundary and the different dislocations. More composition profiles are given in the supplementals (Fig. S4). At the boundary and the dislocations, the composition is Fe_{37.5±1.5} V_{41.4±1.8} Al_{17.5±0.8} C_{1.3±0.4} N_{2.3±0.5} (at.%). Averaged over a 500 million ion data set, with the error corresponding to the 2σ of the counting statistic, the composition is Fe_{49.7±0.01} V_{26.26±0.01} Al_{24.00±0.01} C_{0.013±0.001} N_{0.016±0.005} (at.%). This value is close to the bulk composition of the arc melted sample measured by ICP-OES. No indication for grain to grain variations could be observed, including across different APT specimens.

Fig 2a) EBSD inverse pole figure with [001] reference axis of the melt pool shown in Fig. 1c. Low orientation differences are found. b) EBSD kernel map showing the misorientations of the 2nd nearest neighbor. The scale is set for misorientations between 0° and 2°.
Fig 3a) APT reconstruction showing Fe, V, Al ions as blue, green and orange dots, respectively. A black iso-composition surface for 0.5 at.% (VC, VN, C, N) is shown to visualize precipitation at a LAGB and dislocations. 

b) Detector hit maps at the boundary and on either side of the boundary. The boundary is visible in the second map, indicated by the black arrows. The position of the (111) pole on either side of the boundary is marked by an asterix and given below the maps in detector coordinates. The position can be used to determine the misorientation angle of the boundary to be approximately 1.1°. 

c) Composition profile along the low angle boundary, marked by the black arrow in a). Please note the different scales on the y-axis for the different regions. An enhancement of V, N, and C is found at the grain boundary, indicating VC₃N₅ precipitates.

The observed precipitates can be compared to precipitates found in melt spun Fe₂VA1, as reported earlier [15]. The precipitates observed in melt spun Fe₂VA1 can be observed in SEM images and show sizes of approximately 200 to 300 nm and a thickness of some nm. Contrary, after LSR no precipitation is observed in the SEM images, but only in APT reconstructions since the precipitates are much smaller. Also, the concentration of C and N is much lower than in melt spun Fe₂VA1, where compositions of up to V₆₃.₂±₁.₇N₁₃.₅±₁.₁C₉.₆±₀.₉Fe₈.₂±₀.₈Al₅.₃±₀.₇ were observed. This difference can be attributed to a different purity of the synthesis processes. Vanadium is known for its high affinity to form carbides and nitrides. C and N might be more available in the atmosphere of the melt spinning process compared to arc melting and LSR. While melt spinning results in spherical grains with HAGB, LSR results in elongated grains with LAGB. The different boundaries can influence precipitation due to a different driving force, i.e. boundary energy, which can also change the level of segregation and precipitation.

The resistivity was analyzed within the melt pool at two different LAGBs distinguished by misorientation, and within a bulk HAGB unaffected by the laser remelting. The measurement positions are indicated in the
To obtain absolute values of resistivity from the measured sheet resistance, correction factors are required [25]. However, the irregular shape of the remelted surface prevents deriving corresponding correction factors. Nevertheless, the relative increase in resistivity $\bar{R}$ due to a single GB is obtained as the ratio between resistance across GB and resistance within a single grain. This ratio is reliable when the positions of needles for measuring single- and bi-crystals are close enough to each other (less than the distance between the probing needles). Then the correction factor is similar for both of them, thereby canceling out in the ratio. For each boundary, $\bar{R}$ and the corresponding misorientations determined by EBSD are given in Tab. 1. At the HAGB, the resistivity is enhanced by a factor of 1.14 compared to the neighboring grains due to electron scattering. In contrast, the LAGBs show a resistivity enhancement of 1.04-1.07. These local electrical measurements reveal a reduced influence of the LAGB within the melt pool on resistivity compared to the HAGBs within the original sample. Despite the known dependence of electron scattering with GB structure [20,26], our results are a direct evidence of the minor effect of GBs within the melt pool on the resistivity, relatively to the original materials’ GBs. Yet, the grain size within the melt pool is significantly reduced and thus the relatively high density of LAGB will contribute to an overall enhancement of the resistivity.

Enhancing thermoelectric performance requires minimizing the product of the electrical resistivity and the thermal conductivity. Thus, the enhanced electrical resistivity can be compensated by increased phonon scattering at the boundaries. At room temperature, the mean free path of the electrons is typically on the order of several nanometers, while for phonons it is approximately 2.4 µm.

The impact of grain boundaries of a high-density of 1 µm-grains is assumed to have a stronger influence on the phonons than on the electrons. However, the influence of the observed microstructure on the thermal conductivity could not be analyzed here. In the literature, the impact of dislocations and LAGB has been investigated on Bi$_2$Te$_3$ [27,28] and half-Heusler compound NbCoSn [29]. In these studies, the thermoelectric figure of merit could be enhanced by grain refinement and a high dislocation density [29]. The impact of the phonon scattering was large and could outperform the degraded electrical conductivity. Due to the low electron scattering investigated here at LAGBs and the hypothesized phonon scattering, we can assume that LSR enhances the thermoelectric properties compared to arc melting.

In conclusion, we investigated the microstructure and local electrical resistivity of Fe$_2$VAl treated with laser surface remelting. Within the melt pool, we observed a high density of dislocations and small elongated grains, separated by LAGBs with typical misorientation of 1°–5°. Parallel to the surface, the grain size is approximately 1 µm and therefore smaller than the mean free path of the phonon (approx. 2.4 µm). APT also revealed segregation of vanadium, carbon, and nitrogen towards these defects, likely stabilizing them by lowering their free energy. The electrical

| GB1  | GB 2  | GB 3  |
|------|------|------|
| Misorientation | 2.5° ± 0.3° | 5.3° ± 0.3° | 20.8° ± 0.5° |
| $\bar{R}$ | 1.04 ± 0.03 | 1.07 ± 0.03 | 1.14 ± 0.03 |

Tab. 1: Misorientation and relative increase in the resistivity $\bar{R}$ due to a single GB. The positions of the boundaries are shown in the supplementary Fig. S5.
resistivity change at a LAGB is lower than at a HAGB. Together with the assumed enhancement of the phonon scattering due to the LAGB, the thermoelectric properties are expected to be enhanced by changing the synthesis route to LSR. The flexibility of LSR, i.e. in terms of an adjustable cooling rate, enables further investigations of the impact of the cooling rate on defects and thermoelectric properties.

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Supplemental figures:

![Image](image_url)

**Fig. S1**) optical image of the cross section of several melt pools, treated with LSR. The melt pools are visible on the top of the image, while the lower part shows the sample in as-cast conditions. Cracking appears mainly at grain boundaries of the arc melted sample.
Fig. S2) SEM image of a melt pool of Fe2VAl, treated with laser surface remelting. The area used for the EDX scan is shown. b-d) EDX maps of b) Fe, c) V, d) Al. No compositional changes can be observed in the micron scale.
Fig. S3) EBSD calculation of the grain boundary misorientations angle between 1° an 10°. a) Low angle grain boundaries within the melt pool. The color code of the misorientation angle is given in b). b) Number fraction and color code of the different misorientations angles between 1° and 10°. The misorientation was averaged in an angular width of ± 0.25° around the given value.
Fig. S4) APT reconstruction and composition profiles of different dislocations and the low angle grain boundary. The blue cuboids indicate the region-of-interest in which the profile was calculated. The step size for the calculation was 0.4 nm.
Fig. S5) Positions of the local electrical resistivity measurement. The SEM images including insets show the probes before the measurement. Within the EBSD inverse pole figure (with [001] reference axis) the position of the probes is indicated. a) Grain boundary 1 and 2 within the melt pool, b) grain boundary 3 in the arc melted region. The area shown in a) is indicated by the white square.