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Structure Evolution of Multi-Alloyed Iron Aluminides during Two-Step Annealing

Vera Vodickova (0000-0001-7100-9932), Pavel Hanus (0000-0003-1533-1016), Petra Pazourkova Prokopcakova (0000-0002-9434-6349), Martin Svec (0000-0003-3198-3356)
Faculty of Mechanical Engineering, Technical University of Liberec. Studentská 1402/2, Liberec. Czech Republic.
E-mail: vera.vodickova@tul.cz, pavel.hanus@tul.cz, petra.prokopcakova@tul.cz, martin.svec@tul.cz

The microstructure of single-phase (as-cast) and two-phase (after heat treatment processes) Fe3Al-based alloys doped with silicon, molybdenum, and vanadium/tungsten have been studied. The grain size and phase composition have been determined. The evolution of the secondary phase amount, morphology, and distribution during the heat treatment process has been investigated. Both alloys were heat treated at 1200°C/2 h and, subsequently, at 900 °C. For both alloys, the secondary phase formation started after heat treatment at 900°C /4h, and their amount depended on the annealing time. Vanadium atoms remain in the solid solution, while tungsten atoms partially participate in secondary phase formation.

Keywords: Fe-Al-Si iron aluminides, Molybdenum, and vanadium/tungsten addition, Heat treatment

1 Introduction

In the last few decades, Fe3Al-based iron aluminides have been investigated and developed as a cheaper substitution for high-doped alloys for high-temperature applications. Except for good mechanical properties at higher temperatures, these alloys are characterized by excellent corrosion resistance in oxidizing and sulfidizing environments [1-3].

On the other hand, their relatively low ductility at room temperature is an obstacle to their wider use. Fortunately, mechanical properties at room temperature can be improved mainly by alloying with a third (and other) element, such as chromium, niobium, titanium, or zirconium etc. [4-10]. The crucial point for alloying is how the alloying element acts - i.e. what is its solubility in a particular system - whether it dissolves in the matrix to form a solid solution or whether it participates in the formation of a secondary phase, coherent or incoherent [4, 5].

Silicon is mentioned as one of the elements that affect the high-temperature properties of iron aluminides - adding silicon increases the strength at high temperatures, creep resistance, and oxidation resistance [1-3]

Regarding silicon's influence on iron aluminides' oxidation resistance, it was shown that the oxidation rate of Fe–Al–Si alloys is three to four orders lower than that of Fe–Al and Fe–Si alloys. The cause is the presence of a double oxide layer acting as a protection on the surface: a dense aluminum oxide layer and a layer of iron silicides below it [13]. From the point of view of maintaining corrosion resistance, using elements soluble in the matrix appears to be more effective in avoiding selective corrosion [14 - 16]. For iron aluminides prepared by classical casting, the silicon content is higher than 10 at. % causes an increase in brittleness [17]. The resulting problems - low ductility at room temperature and poor machinability - complicate not only the production but also the subsequent processing of silicon-doped iron aluminides, as well as the preparation of samples for testing. This aspect can be eliminated by using powder metallurgy for the production of silicon–doped iron aluminides, especially in connection with mechanical alloying [18, 19]. Although powder metallurgy processes remain more expensive than conventional casting, current research is mainly focused on them [20-24].

In the case of cast iron aluminides, considerable effort is devoted to researching the influence of alloying elements on the structure and properties of the alloys. Molybdenum has been reported as an additive element improving the high-temperature mechanical properties of Fe3Al-based iron aluminides [1, 25, 17].

Vanadium is one of the elements that increase the transformation temperature [26, 27] and, therefore, has the potential to improve the mechanical properties. Alloying of Fe3Al-based aluminides with vanadium only substantially increases the strength of the single-phase alloys through solid solution hardening [28]. Tungsten alloying has so far been tested mainly for titanium aluminides used in the aerospace industry to improve their oxidation resistance [29].

Except for alloying with suitable elements, a convenient heat treatment affecting the structure can be another possibility to improve the properties of the alloy. Heat treatment can cause the formation of the

secondary phase, and affect its amount, morphology, and distribution. Unfortunately, the heat treatment sometimes tends to be accompanied by significant coarsening of the secondary phase particles, which can lead to a deterioration of mechanical properties [30, 31].

This article aims to describe changes in the structure of cast iron aluminides after a two-step annealing process. The changes in the secondary phase composition, distribution, and morphology, are discussed concerning possible strengthening mechanisms.

2 Experimental Methods

Both investigated alloys were prepared using vacuum induction melting and casting. Table 1 gives the alloys' identification and nominal chemical composition. The Fe3Al-type iron aluminides differ in the addition of vanadium or tungsten. As can be seen from Table 2, a two-step heat treatment with increasing annealing time was used. Basic annealing at 1200°C for 2 hours was the first step for states, and immediately, the samples were annealed at 900°C for 4h, 8h, and 24h gradually.

Tab. 1 *Nominal chemical composition of investigated alloys*

Alloy	Fe	Al	Si	Mo	V	W
FeAl5Si2MoV	bulk	28	5	2	1	-
FeAl5Si2MoW	bulk	28	5	2	-	1

Tab. 2 *The types of heat treatment applied*

Designation	Heat treatment
HT1	1200 °C/2h + 900 °C/4h
HT2	1200 °C/2h + 900 °C/8h
HT3	1200 °C/2h + 900 °C/24h

The microstructure investigation, including the local chemical composition of phases, was carried out by a scanning electron microscope (SEM) Tescan Vega (using Energy Dispersive X-ray Spectroscopy – EDX – performed by Oxford UltimMax 20 detector). Tescan Mira 3 scanning electron microscope was used for the more detailed investigation of structure and specification of phase composition (Oxford UltimMax 65 detector). The grain size measurement was performed through Electron Backscatter Diffraction – EBSD – by Oxford Instruments Symmetry detector. Fractional volumes of secondary particles were determined by image analysis using NIS-Elements software.

3 Results and discussion

3.1 Analysis of FeAl5Si2MoV alloy structure

In the as-cast state, the structure of FeAl5Si2MoV alloy is single-phase: it is formed only by a solid solution, see Fig. 1a. Subsequent annealing at 1200°C/2h + 900°C/4h (HT 1) affects the structure significantly – the plates-like particles of the secondary phase are distributed within the grains as well as along grain boundaries (Fig. 1b).

The prolongation of the annealing time to 8h causes the recordable increase of the volume fraction of particles (almost double, compared to HT1 annealed state), Fig. 1c. A further increase in the fractional volume of particles is observed after the subsequent prolongation of annealing time to 24h, Fig. 1d.

Also, the grain size tends to increase as the annealing time increases. In comparison to as-cast state (grain size 494 μm), the grains become coarser (810 μm) after HT1 (or 828 μm after HT2 resp.), but this coarsening is not so significant after 24h annealing at 900°C – HT3 (646μm), as visible in Fig. 2.

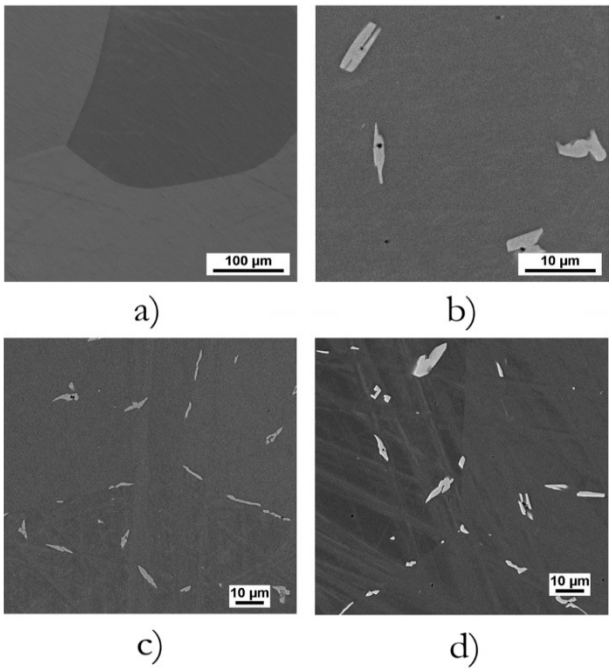

Fig. 1 *a) FeAl5Si2MoV alloy, as-cast, SEM, 20kV, SE; b) FeAl5Si2MoV alloy, HT1, SEM, 20kV, SE+BSE; c) FeAl5Si2MoV alloy, HT2, SEM, 20kV, SE+BSE; d) FeAl5Si2MoV alloy, HT3, SEM, 20kV, SE+BSE*

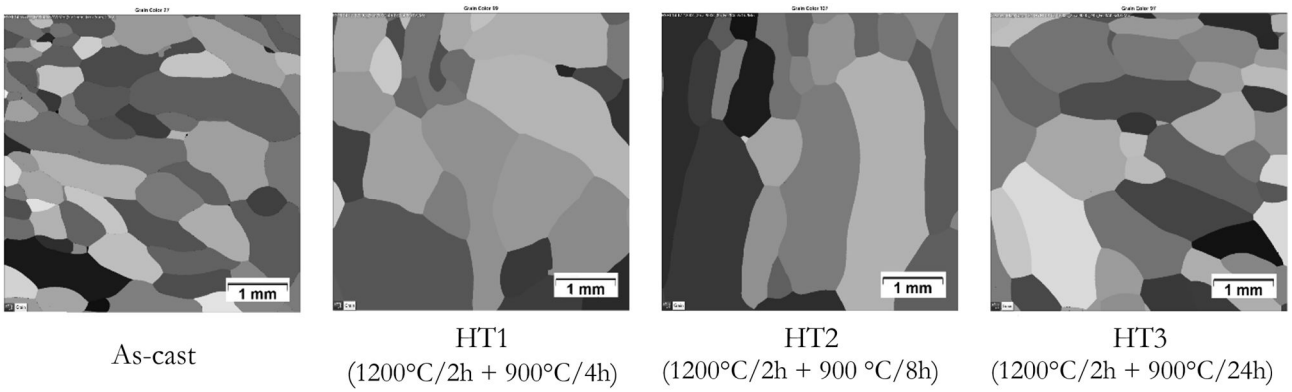

Fig. 2 *FeAl5Si2MoV alloy, EBSD grain maps of different states of structure*

A significant (approximately quadratic) increase in the volume fraction of the secondary phase in the structure of the FeAl5Si2MoV alloy with an increase in the annealing time can be seen from the graph in Fig. 3.

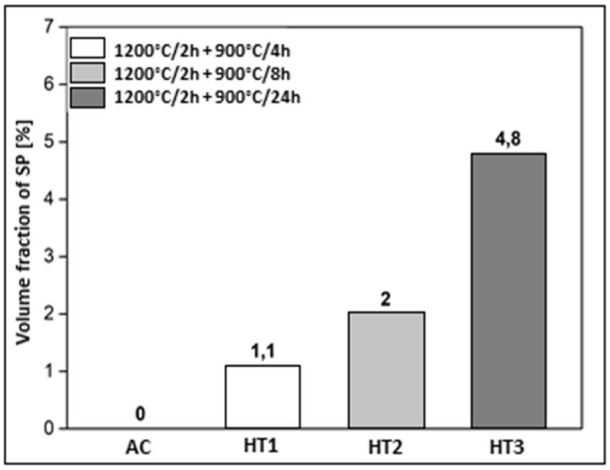

Fig. 3 *The volume fraction of the secondary phase (SP) in the structure of FeAl5Si2MoV alloy depending on the state of the alloy*

The morphology, form of distribution, and composition of the secondary phase particles are not changed significantly during the three types of heat treatment. In addition, no particle coarsening is observed in dependence on annealing time.

As can be seen from the results of EDX analysis (Fig. 4, Fig. 5), silicon and molybdenum participate in the formation of secondary phase particles, while vanadium atoms are dissolved in the Fe-Al matrix.

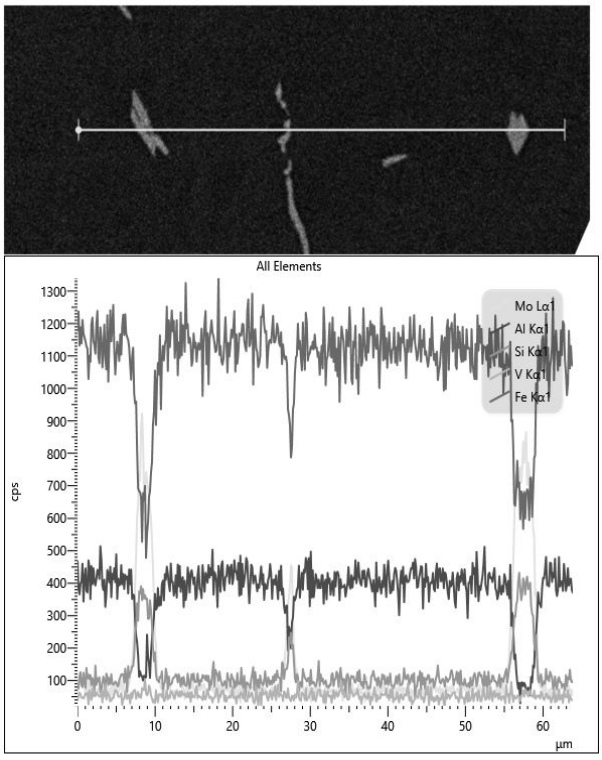

Fig. 4 *Line EDX analysis of FeAl5Si2MoV alloy, HT2*

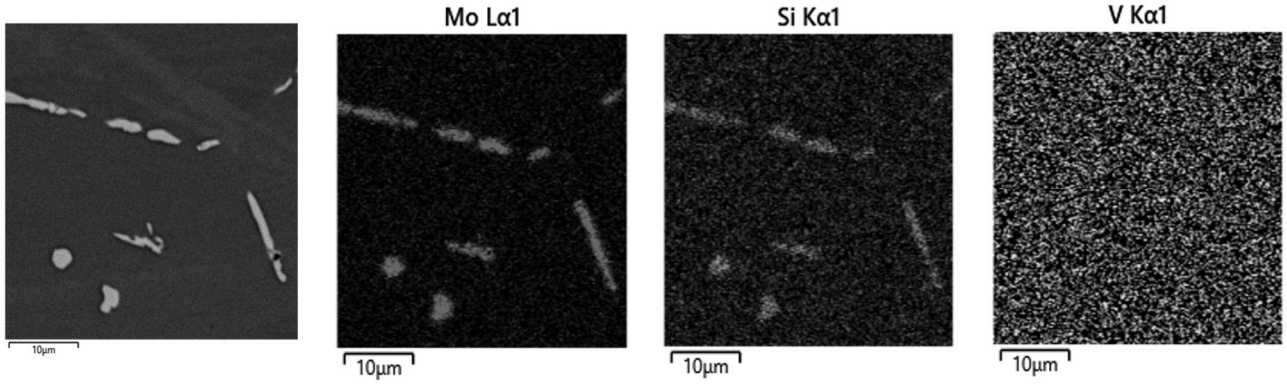

Fig. 5 *EDX analysis (mapping) of secondary phase particles in FeAl5Si2MoV alloy, HT3*

Based on the EDX analysis results (mapping, line, and point analysis), the particles are most likely complex silicides (FeMoSi type). The same type of particles was identified (and verified by XRD analysis) in the structure of this material after long-time annealing [32].

The recorded increase in volume fraction of precipitates from 1,1 % (after HT1) to 4,8 % (after HT3) drained molybdenum and silicon atoms from the matrix. Nevertheless, vanadium atoms remaining in a solid solution can further strengthen the matrix. On the other hand, the secondary phase particles do not contribute to total strengthening given their form, size, and frequency of occurrence. These sharp-edged particles can act as sources of cracks when loading the material.

3.2 Analysis of FeAl5Si2MoW alloy structure

Similar to vanadium doped alloy, the structure of as-cast FeAl5Si2MoW alloy is single-phase only, and all of the additives are dissolved in the matrix. No secondary phase particles are noticed in the as-cast state see Fig. 6a. Before heat treatment application, the structure is significantly coarse-grained.

In the course of HT1 (1200°C/2h + 900°C/4h), the precipitation of the secondary phase starts. The particles are distributed inside the grains and also line the grain boundaries (Fig. 6b). With the annealing time prolongation to 8h and 24h (structure detail in Fig.6c, Fig. 6d), no significant change in secondary phase distribution was recorded.

In the case of FeAl5Si2MoW alloy, grain size increase with the shorter annealing time (HT1, HT2) was not noticed. The values measured by EBSD after the first two types of heat treatment (763 m HT1, or 822 μm after HT2) are comparable to the as-cast state value (768 μm). However, after the longest annealing (HT3), the grain size increased over a micron (1030 μm), Fig. 7.

Compared to the vanadium-doped alloy, the particles of the secondary phase in the FeAl5Si2MoW alloy are distributed with a higher density - this corresponds to a higher fractional volume of the particles. The increase in the fractional volume of the secondary phase with increasing annealing time is not so progressive as for vanadium-doped alloy, and the values for states after longer annealing (HT2, HT3) are comparable within the measurement error (graph in Fig. 8).

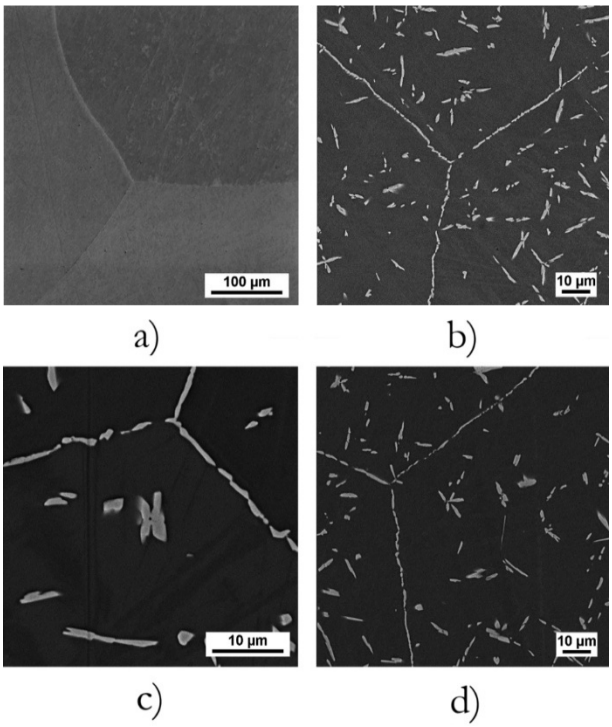

Fig. 6 *a) FeAl5Si2MoW alloy, as-cast, SEM, 20kV, SE; b) FeAl5Si2MoW alloy, HT1, SEM, 20kV, SE+BSE; c) FeAl5Si2MoW alloy, HT2, SEM, 20kV, SE+BSE; d) FeAl5Si2MoW alloy, HT3, SEM, 20kV, SE+BSE*

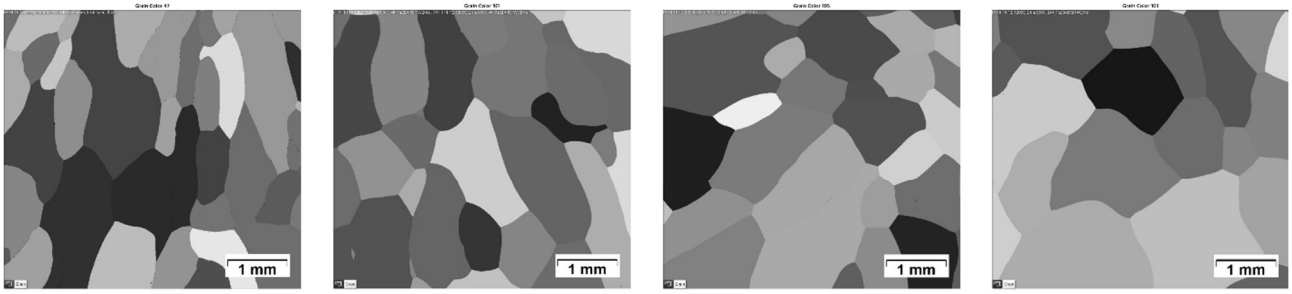

Fig. 7 *FeAl5Si2MoW alloy, EBSD grain maps of different states of structure*

As can be seen in Fig. 9, tungsten participates in the formation of the secondary phase in the FeAl5Si2MoW alloy. Similar to vanadium-doped alloy, the particles in the structure of FeAl5Si2MoW alloy also can be complex silicides but have a low tungsten content - FeMo(W)Si type based on the EDX analysis results, Fig. 9. The same type of particles was identified (and verified by XRD analysis) in the structure of tungsten-doped alloy after long-time annealing [32].

Also, in the case of FeAl5Si2MoW alloy, precipitation of silicide-type particles caused the depletion of the solid solution. As a result of the heat treatment used, molybdenum, silicon and tungsten atoms were removed from the matrix (tungsten only in a small part), which probably led to a decrease in the proportion of solid solution strengthening in total strengthening. However, it is not excluded that this alloy may have a stronger contribution from incoherent precipitates, owing to the particle´s size, morphology, and distribution way. The fine Mo(W)Si-based particles are distributed in the matrix more equally than in the case of vanadium-doped alloy. In addition, by increasing the annealing time, no visible coarsening of particles occurs, so it is not excluded that they could act as obstacles for the movement of dislocations.

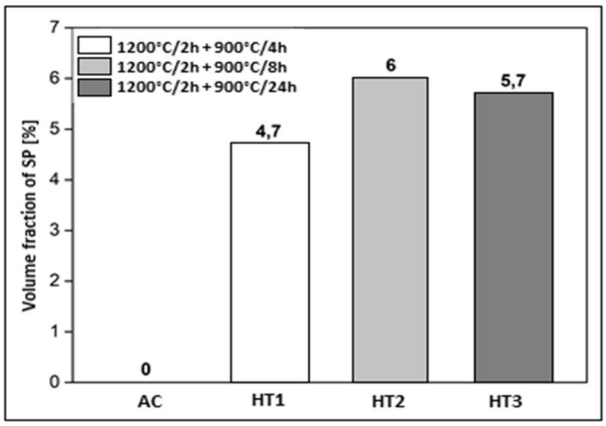

Fig. 8 *The volume fraction of the secondary phase (SP) in the structure of FeAl5Si2MoW alloy depending on the state of the alloy*

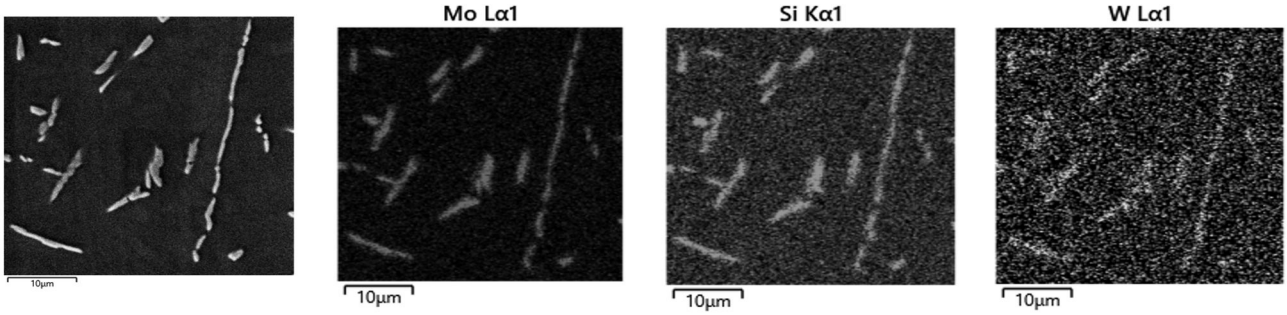

Fig. 9 *EDX analysis (mapping) of secondary phase particles in FeAl5Si2MoW alloy, HT3*

4 Conclusion

For FeAl5Si2MoV alloy, a progressive increase in the FeMoSi-based secondary phase volume fraction was recorded with increasing annealing time. Vanadium does not participate in the formation of the secondary phase (even after 24 hours of annealing). It remains fully dissolved in the matrix and can participate in strengthening.

In the case of FeAl5Si2MoW alloy, the precipitation of the secondary phase in the form of a fine needle-like dispersion occurs after HT1. Unlike vanadium-doped alloy, tungsten participates in the formation of the secondary phase particles.

For both alloys, the grain size is influenced by applied annealing. It appears to be increasing with annealing time, except for the longest annealing (HT3) of FeAl5Si2MoV alloy. However, the influence of considerable unevenness in grain size must be taken into account when interpreting the results of EBSD measurement.

Both types of secondary phase particles (complex silicides) are very stable during stepped annealing. There is neither dissolution nor significant coarsening of the particles. It can be assumed that strengthening by incoherent precipitates also contributes to the total strengthening of alloys alloyed with vanadium or tungsten, more significantly in the FeAl5Si2MoW alloy.

A positive influence of used annealing on high-temperature mechanical properties (e.g. alloy strengthening) can be expected especially from FeAl5Si2MoW alloy.

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