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EFFECT OF PRELIMINARY ACTIVATION OF TiAl POWDER ON THE PROCESS OF MECHANOCHEMICAL SYNTHESIS OF (Fe, Ti)$_3$Al INTERMETALLICS

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ABSTRACT

The effect of mechanical activation of TiAl powder on the structural and phase transformations in mechanochemical synthesis of the powder mixture of the composition 60.8Fe + 39.2TiA1, intended to produce Fe_3Al intermetallics, alloyed with titanium was studied. Using a semi-empirical Miedema's model, the changes of Gibbs energy for the binary Ti–Al, Fe–Ti and Fe–Al systems were calculated. The results showed that the driving force for the formation of intermetallic phases for all the binary systems is higher as compared to the formation of solid solutions and amorphous phases. A range of compositions was established, at which the formation of amorphous phases in the binary Ti–Al and Fe–Al systems is possible. Carrying out the mechanical activation of TiAl intermetallic powder in a high-energy planetary mill allowed reducing the size of a coherent scattering region from 280 to 9 nm with a partial amorphization. The formation of particles with a homogeneous microstructure consisting of intermetallic phase (Fe, Ti)$_3$Al and Laves phases — Fe_2Ti was revealed in the process of mechanochemical synthesis of a powder mixture 60.8Fe + 39.2 TiAl when using nanostructural TiAl powder. The change in the region of coherent scattering of powders of 60.8Fe + 39.2TiAl mixture, produced by the method of mechanochemical synthesis, was evaluated and it was established that interaction of a nanostructural powder TiAl with Fe begins to occur when the size of a coherent scattering region becomes <70 nm. The resulting product has an amorphous-nanocrystalline structure with a size of the coherent scattering region of <15 nm. The use of the developed powder in thermal spraying technologies will allow producing coatings based on Fe_3Al intermetallics with a nanocrystalline structure, a higher modulus of elasticity and ductility.

KEYWORDS: mechanochemical synthesis, mechanical activation, titanium aluminide, semi-empirical Miedema's model, nanocrystalline structure, amorphous phase

INTRODUCTION

One of the modern technologies for producing powders for thermal spraying (TS) is the method of mechanochemical synthesis (MChS). This method, taken into account its simplicity and cheapness, has found its use for producing nanostructural powders of iron aluminide [1]. The combination of high strength and corrosion properties of iron aluminides makes these alloys promising materials for using as protective coatings on the blades and housings in the compressor of jet engines, design elements of aircrafts, heating elements, in heat exchangers, in components of nuclear reactors, on automobile piston valves, etc. [2, 3]. The main advantage of iron aluminides as compared to heat-resistant nickel alloys and stainless steels is the availability and cheapness of the basic iron component, as well as the ease of their machining. Introduction of iron of the third element to aluminide will allow increasing their mechanical characteristics. As alloying components, Ti, V, Cr, C, etc. are used [4]. The use of titanium as an alloying element leads to the formation of an intermetallic compound Fe_2TiA1 ($L2_{1,}$ triple equivalent Fe_3Al ($D0_3$) structure), which allows increasing the temperature of a phase transition $L2_1$ → B2 from 550 to 1215 °C and stabilizing the ordered structure to higher temperatures as compared to binary system [5].

About the formation of an intermetallic compound (Fe, Ti)$_3$A1 during the process of MChS of powder mixtures of the stochiometric composition $Fe_{50}A1_{25}Ti_{25}$ (at.%) was reported in [1, 6]. It was found that the process of formation of (Fe, Ti)$_3$Al intermetallics depends on the source materials. While using the powders of Fe, Ti and Al as the source materials, the formation of intermetallics passes through the stages of forming layered composites of Fe/Al/Ti with their subsequent transformation into a solid Fe(Al, Ti) solution, and then into the intermetallic phase $D0_3$ (Fe, Ti)$_3$Al [6]. In the case of using TiAl-Fe as the source powders, the phase transformations are accompanied by the formation of ferrotitanium followed by dissolving of Al in its lattice up to the formation of (Fe, Ti)$_3$Al intermetallics [1].

The use of preliminary mechanical activation (MA) of the source powders allows increasing the reactivity of solid substances, which is associated with the accumulation of crystalline structure defects and an increase in the enthalpy of a material [7]. The use of MA in the technology of self-propagating high-temperature synthesis (SHS) allows expanding the capabilities of gas-free burning for a high-temperature synthesis by increasing the burning rate and a significant decrease in the reaction initiation temperature. The burning rate during MA of the powder mixture 27Ti + 13B + 60Cu (wt.%) increases by ~42 % (from 6.25 to 14.8 mm/s), and that of the the mixture 22.4B_4C + 77.6Ti (wt.%) grows by ~49 % (from 11 to 22.5 mm/s) [8, 9].

The aim of this work was to study the influence of preliminary mechanical activation of TiAl intermetallic powder on structural and phase transformations occurring in the process of MChS of the powder mixture 60.8Fe + 39.2TiAl, intended to produce Fe_3Al intermetallics alloyed with titanium.

MATERIALS AND RESEARCH PROCEDURES

As the source materials to produce the powder of the Fe–TiAl system, iron powder and TiAl powder were used (Table 1).

Table 1. Characteristics of source powders used to produce MChS powder of the Fe–TiAl system

Powder	Grade	Chemical composition, wt.%	Particle size, μm
Fe	PZhR	Fe > 98.5	80–100
TiAl	PVT65Yu35	Ti – 67.5; Al – 32.5	<20 μm

The amount of TiAl intermetallic powder, introduced into the mixture with iron powder, amounted to 39.2 wt.%, which, at such a ratio of components, allows producing a single-phase product based on Fe_3Al intermetallic in the MChS process [10].

MA and MChS processes were carried out in a planetary mill (Activator 2S1) at the drum rotation speed of 1500 rpm, the ratio of balls mass to powder mass of 10:1, the medium is air. In order to eliminate sticking of the processed charge on the grinded bodies and drum walls, as well as to intensify the process of synthesis of new phases, a surface-active substance (SAS) — oleic acid ($C_{17}H_{33}COOH$) in the amount of 0.5 wt.% was added to the mixture. The time of preliminary MA was 3 h and the time of MChS was 5 h.

The sequence of structural and phase transformations during MChS in the Fe–Al–Ti system using MA of TiAl powder was studied on the particles removed from the reactors after certain time intervals (0.5, 1.5 and 3 h).

The chemical analysis of the produced composite powders (CP) was studied in the JSM-6390LV scanning electron microscope (JEOL, Japan) with the attachment for energy dispersive analysis INCA ENERGY (Oxford Instruments, Great Britain), in the mode of secondary electrons in a low (10^{-4} Pa) vacuum with an accelerating voltage of 20 kV.

X-ray diffraction phase analysis (XRD) was performed using the Ultima IV diffractometer (Rigaku, Japan) in CuK_α-radiation with a graphite monochromator. The phase identification was carried out using the international database ICDD PDF-2 or PDF-4 by computer processing of the received digital data. Using the PDXL program for harmonic analysis, provided by the Rigaku X-ray unit, an evaluation of the coherent scattering region (CSR) was carried out.

THERMODYNAMIC EVALUATION OF THE POSSIBILITY FOR PROCEEDING REACTION IN THE Fe–Ti–Al SYSTEM

The evaluation of the possible reactions proceeding in the Fe–Ti–Al system was carried out for the binary Ti–Al, Fe–Ti and Fe–A1 systems with the calculation of change in the Gibbs energy for the crystalline (intermetallic, solid solution) and amorphous states with a continuous series of component concentrations. The analysis was performed using Miedema's semi-empirical model for binary systems (Figure 1) [11, 12].

The obtained results indicate that the driving force for the formation of intermetallics in all the ranges of compositions for binary systems is higher as compared to the solid solution and the amorphous state. For the amorphous state at certain compositions of binary systems, there are positive values of the Gibbs energy (Table 2).

Based on the carried out calculations, it can be noted that in the Fe–Ti–Al system, the formation of Ti–Al (when Al < 85 mol.%) and Fe-Ti (when Ti > 85 mol.%) compounds is possible. For the Ti–Al and Fe–A1 systems in the range of 32 mol.% < X_{A1} <

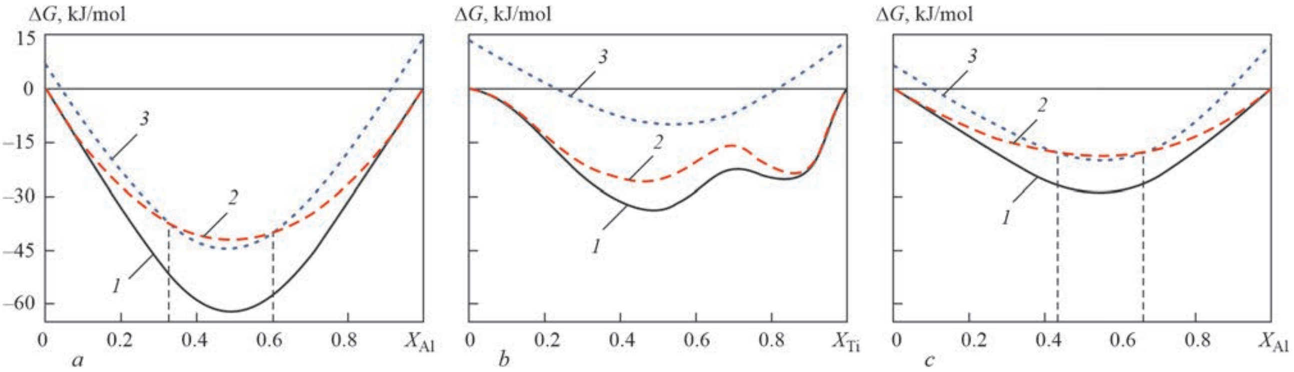

Figure 1. Change in Gibbs energy in the Ti–Al (*a*), Fe–Ti (*b*) and Fe–Al (*c*) systems for: *1* — intermetallics; *2* — solid solutions; *3* — amorphous state

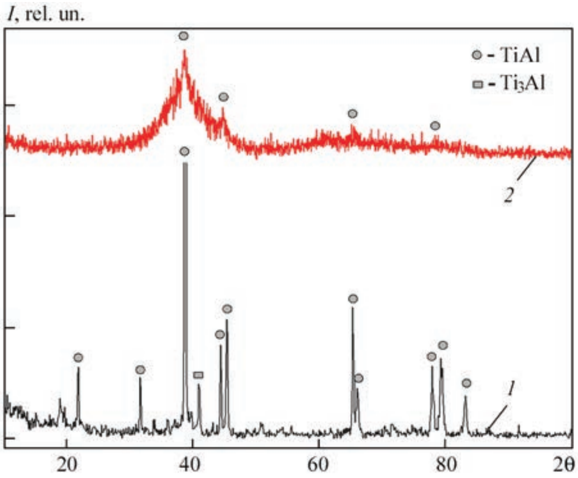

Figure 2. X-ray patterns of TiAl source powder (*1*) and TiAl powder after mechanical activation (within 3 h) (*2*)

< 76 mol.%, the free Gibbs energy for the formation of compounds in the amorphous state is lower than for solid solutions, which indicates the possibility of the amorphous phase formation in these systems [13].

Transferring TiAl into the amorphous state will allow reducing its thermodynamic stability, which can contribute to the intensification of the process of interaction of TiAl with Fe in the MChS process.

RESEARCH RESULTS AND THEIR DISCUSSION

Using the XRD method, it was established that MA of the source TiAl powder during 3 h leads to the broadening of diffraction lines and a decrease in their intensity. A strong blurring of peaks at large angles makes their identification difficult. The calculation of CSR showed a decrease in the average value from 280 to 9 nm. The appearance of a "halo" on X-ray patterns indicates a partial amorphization of the powder (Figure 2).

Table 2. Ranges of compositions, in which the value ΔG of the amorphous phase formation is positive

System	Composition range, mol.%
Fe–Al	$X_{Al} < 0.05$ and $X_{Al} > 0.95$
Fe–Ti	$X_{Al} < 0.2$ and $X_{Al} > 0.88$
Ti–Al	$X_{Al} < 0.03$ and $X_{Al} > 0.97$

The microstructure and appearance of Fe–TiAl powder particles produced by the MChS method at different time of processing are presented in Figure 3.

Analyzing the appearance of the powders, it is possible to note the developed surface of the particles, which indicates that the formation of conglomerates in the MChS process occurs due to welding of small particles of the source components with each other.

Studying the microstructure of particles produced at different stages of MChS, it is possible to note the formation of thin lamellar conglomerates at the early stages and the homogenization of the structure at the later stages.

With the use of X-ray spectral microanalysis, the chemical composition of the powder particles produced at different durations of the MChS process was determined (Table 3). There is no significant difference observed between the calculated composition of the mixture 60.8Fe + 39.2TiAl (wt.%) and the actual chemical composition of the resulting product. Only the presence of oxygen in the amount of 2–5 % is noted, which is associated with the MChS process carried out in air.

The interaction of Fe with a nanostructured TiAl powder in the MChS process takes place in several stages. At the initial stages, refinement of iron takes place. The formation of an amorphous "halo" at the place of the X-ray peak at $2\Theta = 38°$ indicates the amorphization of TiAl. Further, the merging of an amorphous "halo"

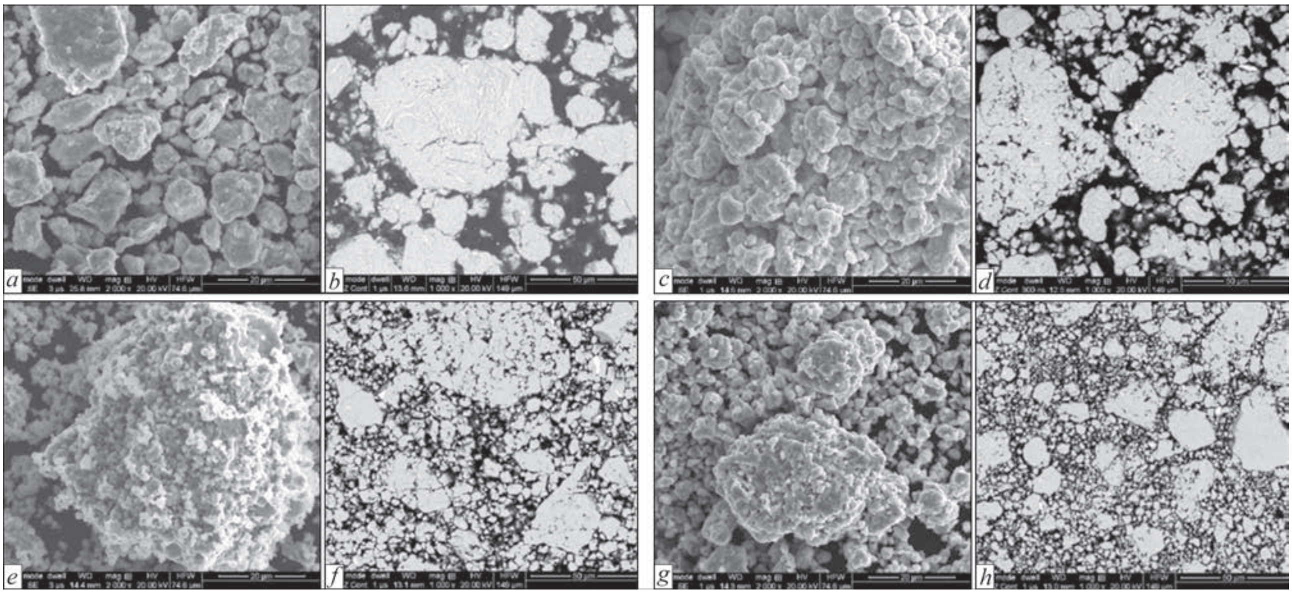

Figure 3. Appearance (*a*, *c*, *e*, *g*) and microstructure (*b*, *d*, *f*, *h*) of particles of a composite powder produced by the MChS method from mixture (wt.%) 60.8Fe + 39.2TiAl (mechanically activated TiAl) within 0.5 h (*a*, *b*); 1.5 h (*c*, *d*); 3 h (*e*, *f*) and 5 h (*g*, *h*)

Table 3. Chemical composition of composite powder particles at different stages of processing the mixture 60.8Fe + 39.2TiAl (wt.%)

Processing time, h	Content of elements, wt.%			
	Fe	Ti	Al	O
Source composition	60.8	26.5	12.7	–
0.5	57.85 ± 1.45	25.05 ± 0.46	14.71 ± 0.22	2.39 ± 0.76
1.5	62.03 ± 1.51	26.13 ± 0.30	9.24 ± 3.65	2.60 ± 0.42
3	53.71 ± 4.38	23.65 ± 1.45	18.27 ± 2.74	5.04 ± 1.27
5	55.38 ± 3.20	24.41 ± 0.91	14.97 ± 0.40	5.24 ± 0.38

of TiAl with the diffraction maximum of Fe and a mutual overlapping of the diffraction lines of TiAl and Fe is observed. This indicates the formation of a ternary intermetallic (Fe, Ti)$_3$Al compound. At the same time, a strong blurring and a low intensity of Fe peaks at large angles (2Θ > 70°) make their identification difficult. As a result of the interaction of Ti with Fe, after 3 h of processing, a diffraction peak appears in the range of angles 2Θ = 36–38°, indicating the formation of Fe$_2$Ti compound (Laves phase) (Figure 4).

Thus, schematically, the structural and phase transformations in the MChS process of the mixture 61Fe + 39TiAl in the case of using intermetallic TiAl powder with CSR = 9 nm can be represented as follows:

$$\begin{gathered}\mathrm{Fe(CSR=276\,nm)+TiAl(CSR=9\,nm)}\rightarrow\\ \xrightarrow{0.5\mathrm{h}}\mathrm{Fe(CSR=170\,nm)+TiAl_{amorph.}}\rightarrow\\ \xrightarrow{+1.0\mathrm{h}(\Sigma 1.5\mathrm{h})}\mathrm{Fe-TiAl(CSR=54\,nm)}\rightarrow\\ \xrightarrow{+1.5\mathrm{h}(\Sigma 3.0\mathrm{h})}\mathrm{(Fe,Ti)_3Al(CSR=25\,nm)}+\\ +\mathrm{Fe_2Ti_{traces}}\xrightarrow{+2.0\mathrm{h}(\Sigma 5.0\mathrm{h})}\\ \rightarrow\mathrm{(Fe,Ti)_3Al(CSR\sim10\,nm)+Fe_2Ti(CSR\sim15\,nm)}.\end{gathered}$$

Comparing the scheme of structural and phase transformations occurring during the MChS process using unactivated TiAl powder with CSR = 280 nm, it can be noted that unlike the mixture with a nanostructured TiAl powder, an interaction of titanium with iron occurs with the formation of ferrotitanium, dissolution of aluminium in the ferrotitanium lattice and formation of intermetalic (Fe, Ti)$_3$Al [1]:

$$\begin{gathered}\mathrm{Fe(CSR=276\,nm)+TiAl(CSR=280\,nm)}\rightarrow\\ \xrightarrow{0.5\mathrm{h}}\mathrm{Fe(CSR=175\,nm)}+\\ +\mathrm{TiAl(CSR=68\,nm)}\rightarrow\\ \xrightarrow{+1.0\mathrm{h}(\Sigma 1.5\mathrm{h})}\mathrm{Fe(CSR=68\,nm)}+\\ +\mathrm{TiAl(CSR=51\,nm)}+\\ +\mathrm{FeTi_{traces}}\xrightarrow{+1.5\mathrm{h}(\Sigma 3.0\mathrm{h})}\text{solid solution Al in}\\ \mathrm{FeTi(CSR=44\,nm)}\xrightarrow{+2.0\mathrm{h}(\Sigma 5.0\mathrm{h})}\\ \rightarrow\mathrm{(Fe,Ti)_3Al(CSR\sim30\,nm)}.\end{gathered}$$

Evaluation of the change in CSR on the broadening of the X-ray lines of iron at the initial stages of the MChS process and (Fe, Ti)$_3$Al after 5 h of processing the Fe + TiAl mixture in a planetary mill showed that the use of a nanostructured TiAl intermetallics as a source powder leads to producing a final product with a size of CSR <15 nm (Figure 5). The size of CSR of the (Fe, Ti)$_3$Al phase in the case of using an intermetallic powder with a size of CSR = 280 nm after 5 h of processing reaches ~30 nm.

Analyzing the changes in the phase composition and CSR at different stages of mixture processing, it can be noted that merging of the X-ray peaks of TiAl

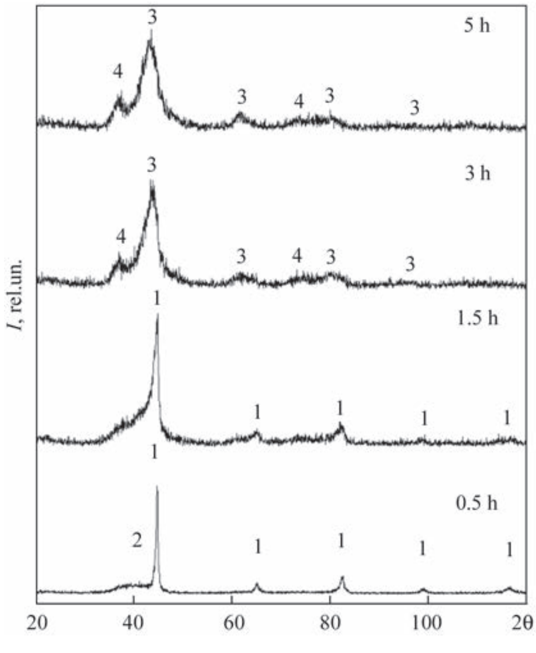

Figure 4. X-ray patterns of MChS powders of the composition 61Fe + 39TiAl (when using nanostructured TiAl powder): *1* — Fe; *2* — TiAl; *3* — (Fe, Ti)$_3$Al; *4* — Fe$_2$Ti

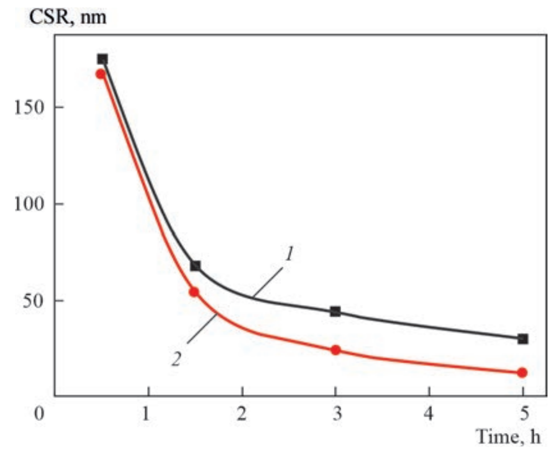

Figure 5. Change in CSR depending on time of MChS of 61Fe+39TiAl mixture (*1* — TiAl, CSR — 280 nm; *2* — TiAl, CSR — 9 nm)

and Fe after 1.5 h of processing occurs when the size of the crystallites becomes <70 nm.

Thus, the use of a preliminary mechanically activated TiAl powder for producing intermetallic (Fe, Ti)$_3$Al powder by the MChS method allows intensifying the process of refining the structure with a reduction in the size of CSR by 1.3 times after 1.5 h of processing (from 68 to 54 nm), and by three times after 5 h of processing (from 30 to 10 nm).

The developed powder of (Fe, Ti)$_3$Al intermetallics can be used in the technology of thermal spraying of intermetallics of coatings with a nanocrystalline structure, increased mechanical characteristics (Young modulus and hardness) and high indices of ductility.

CONCLUSIONS

1. Using the technology of mechanical activation of TiAl intermetallic powder, a nanostructured powder with CSR of ~9 nm was produced.

2. The process of structural and phase transformations occurring in the process of mechanochemical synthesis in a powder mixture of iron and a nanostructured TiAl intermetallic powder was studied. The mechanism of formation of (Fe, Ti)$_3$Al intermetallic consists of producing thin lamellar conglomerates of Fe and TiAl, the subsequent homogenization of the powder microstructure and synthesis of the intermetallic (Fe, Ti)$_3$Al phase (CSR ~ 10 nm) and Laves phase Fe$_2$Ti (CSR ~ 15 nm).

3. It was revealed that the use of a preliminary mechanically activated TiAl powder to produce intermetallic (Fe, Ti)$_3$Al powder by the MChS method allows intensifying the process of refining the structure, which is confirmed by a reduction in the size of CSR after 1.5 h of processing by 1.3 times (from 68 to 54 nm), and by 3 times after 5 h of processing (from 30 to 10 nm).

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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