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Unidirectional solidification of Ni-Mo-Al eutectic alloys

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The composition triangle of the Ni–Mo–Al ternary system contains a monovariant trough between the γ' (Ni_3Al)–α(Mo) pseudobinary eutectic and a guessed γ(Ni)–γ' (Ni_3Al)–α(Mo) ternary eutectic. Alloys with compositions on this trough were directionally solidified at various growth rates. The microstructure of the alloys consists of fine Mo fibres of rectangular cross-section in an Ni_3Al/Ni matrix. The determined crystallographic relationship does not correspond to an interface of low lattice mismatch. The eutectic trough strongly extends towards increasing Mo contents so that the volume fraction of the Mo fibres varies between 18 and 25% dependent on composition. It was not possible to determine the position of a ternary eutectic γ–γ'–α because the liquidus temperatures along the trough are almost equal and the distribution of the three phases is strongly dependent on the growth rate.

1. Introduction

Nickel base alloys with aluminium and refractory metals of IV A-VI A groups of the Periodic Table are most commonly used as materials for high temperature application. Besides these highly developed superalloys, a new group of alloys has been recognized in the last 10 years as potential candidates for higher metal operation temperatures. These are the so-called *in situ* composites produced by unidirectional solidification of eutectic alloys.

Pseudo-eutectic and multivariant alloys based on the systems Ni/Ni_3Al–Ni_3Nb(γ/γ'–δ), (Co, Cr)–TaC and (Co, Cr)–(Cr, Co)$_7$C$_3$ [1] have been shown to possess better stress rupture and fatigue properties than the best current superalloys at temperatures above 800° C. Other systems have not been explored in so much detail presumably because of missing phase diagram data.

Of special interest are eutectics of ternary systems based on nickel, aluminium and a refractory metal. Because of the ductility of the Ni_3Al(γ') phase at room temperature, pseudobinary and ternary eutectic alloys were investigated several years ago. Thompson and Lemkey [2] have determined the properties of eutectics in the systems Ni–Al–Nb, Ni–Al–Ti and Ni–Al–Zr while eutectic alloys of Ni–Al–Ta have been developed by Hubert *et al.* [3].

Only little attention has been given to the systems containing Ni_3Al and VI A group metals (Cr, Mo, W). Apart from short note on the Ni_3Al–Mo(γ'–α) eutectic [4] no further work on these systems has been published until now. Therefore, a programme was chosen to examine possible pseudo-eutectic alloys in the three systems Ni–Al–{Cr, Mo, W} with Ni_3Al as one of the constituent phases.

2. Phase diagrams

The most interesting system with respect to oxidation resistance should be Ni–Al–Cr, but an inspection of the literature revealed that no two-phase equilibria between Ni_3Al and chromium-containing phases are formed by a reaction from the melt. Taylor and Floyd [5] have found that a two-phase region between γ'(Ni_3Al) and α(Cr) created by a 2/2 solid state reaction from γ(Ni) + β(NiAl) during cooling is only stable below about 1000° C.

The ternary system Ni–Al–Mo has been the subject of several different phase diagram investigations. Isothermal sections at temperatures between 1200 and 600° C [6–9] contain a three-phase region of γ(Ni)–γ'(Ni_3Al)–α(Mo). A polythermal section Ni_3Al–Mo is reported by Pryakhina *et al.* [9] who found a four-phase reaction γ(Ni) + β(NiAl) $\rightarrow$ γ'(Ni_3Al) + α(Mo) at 1265° C. This result is in contradiction to the observed eutectic behaviour of Ni_3Al–Mo [4].

The phase diagram of Ni–Al–W has been determined as isothermal sections at 1200 and 800° C [10]. At these temperatures, the W-rich γ solid solution is in equilibrium with the β(NiAl) phase, which suggests that Ni_3Al is not in equilibirum with W-containing phases, similar to the Ni–Al–Cr system above 1000° C.

These differences between the two-phase regions of the low Al parts of the systems Ni–Al–(Cr, Mo, W) reduced the investigations to the system Ni–Al–Mo. Molybdenum is also known to be a better solid solution strengthener at higher temperatures than tungsten, the latter additionally being disadvantageous because of its high density.

It should be mentioned that an advanced turbine vane alloy, NX 188 [12], is located by its composition in the γ–γ'–α field of the Ni–Al–Mo system. The microstructure of this alloy shows that its excellent stability and strength in the directionally solidified condition is due to γ' precipitation and Mo solid solution strengthening. Increasing the molybdenum content should provide further strengthening by *in situ* generation of the Mo reinforcing phase.

3. Experimental procedure

Alloys of different compositions were produced by induction melting of the elements (Ni 99.2%, Mo 99.7%, Al 99.9%) under argon atmosphere. Bars of about 0.5 cm diameter and up to 40 cm long were prepared by sucking a 50 g alloy melt into silica tubes. By applying this method, generally no reaction between the liquid alloy and the tubes occurred.

Unidirectional solidification was achieved by a vertical Bridgman technique using a rhodium resistance furnace. The ingots were placed in thin wall alumina tubes and were melted in a high purity helium atmosphere. Heat transfer from furnace to the sample was improved by a cylindrical graphite block. Cooling of the solidfied portion was conducted by a close fitting water-cooled copper toroid. In this way temperature gradients of 100 to 200° C cm^{-1} were achieved. Solidification was performed by moving the alumina crucible downwards with velocities in a range 0.5 to 20 cm h^{-1}.

All solidified samples contained a minimum length of 8 cm which showed controlled parallel growth. In most cases no reaction between melt and crucible material was observed. A portion of the material was annealed at a temperature of 1100° C in sealed silica tubes in order to prove structural stability.

The alloys were characterized by metallographic and X-ray methods. Liquidus temperatures were determined by DTA measurements. Microanalysis was carried out by an energy dispersive X-ray system applied to a scanning electron microscope.

4. Results and discussion

4.1. Microstructure

The experiments were started using the composition given by Thompson and Lemkey [4]: 65.7 at.% Ni, 16.7 at.% Mo, 17.6 at.% Al (wt%: 65/27/8). This composition is not exactly situated on the two-phase region determined by Guard and Smith [6] and Markiv *et al.* [8], but it became evident that in alloys with higher Al contant, a third phase (NiAl) was present. As NiAl is brittle and, therefore an undesirable constituent, the concentrations of Al were confined to lower values.

In order to find alloys with eutectic microstructure consisting of γ/γ'–α, alloys with 13 at.% Al and different Mo contents were produced. The compositions are presented in Fig. 1, together with the equilibria of the interesting part of the isothermal section of the Ni–Al–Mo phase diagram after Markiv *et al.* [8].

The results show that compositions revealing eutectic microstructure are located on the dashed curve represented in Fig. 1. This curve obviously is a monovarient trough which extends between the pseudobindary eutectic γ'(Ni_3Al)–α(Mo) and a supposed ternary eutectic γ(Ni)–γ'(NiAl)–α (Mo). It was not possible to locate the exact composition of this ternary eutectic by extrapolation of DTA measurements because the liquidus temperatures of alloys lying on the monovariant valley were all the same (1307° C) within the accuracy of measurements.

The microstructure of the directionally solidified alloys shows very fine faceted Mo fibres with rectangular cross-section in the nickel–aluminium matrix. Typical pictures of the pseudobinary com-

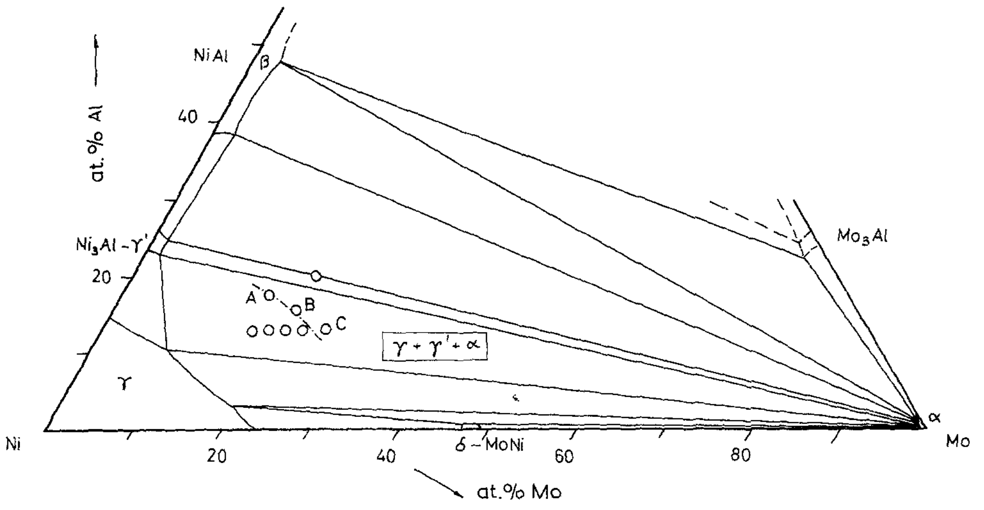

Figure 1 Isothermal section of the Ni–Al–Mo phase diagram at 1000° C (after [8]). Compositions of investigated alloys and projection of the monovariant trough.

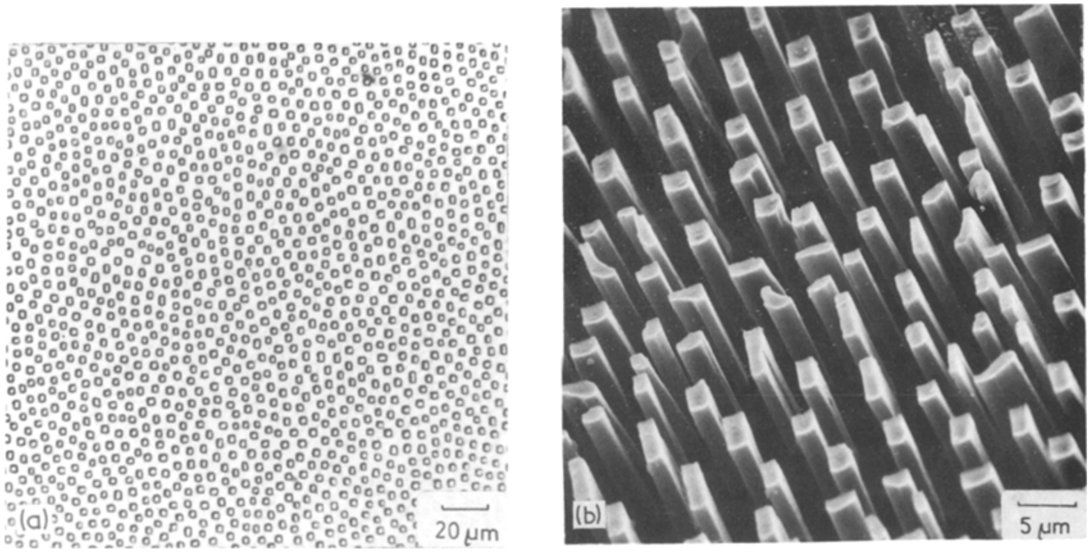

Figure 2 Metallographical sections of directionally solidified Ni_3Al–Mo pseudobinary eutectic alloy A ($Ni_{65.7}Mo_{16.7}Al_{17.6}$) transverse to the growth direction ($R = 0.3\,\mathrm{cm\,h^{-1}}$). (a) Polished sample; (b) scanning micrograph of deep-etched surface showing Mo fibres.

position $\gamma'(Ni_3Al)$–$\alpha(Mo)$ are represented in Fig. 2.

The virtually infinite length of the parallel-grown Mo fibres is shown in Fig. 3 which is produced by etching the matrix away. The plane γ'–α interfaces indicate a strong crystallographic relationship between fibres and matrix. This relationship was determined by X-ray rotating crystal and Weissenberg patterns around the growth direction as the rotation axis. It has been found that the following relations exist:

$$\text{growth direction} \parallel [0\,0\,1]_{Ni_3Al} \parallel [0\,0\,1]_{Mo}$$

$$\text{interfaces} \parallel (1\,0\,0)_{Ni_3Al} \parallel (1\,1\,0)_{Mo} \text{ and}$$

$$(0\,1\,0)_{Ni_3Al} \parallel (\bar{1}\,1\,0)_{Mo}.$$

An inspection of the distribution of atoms on the eutectic interfaces shows that there is poor conformity between stacking sequences normal to the interface and atomic spacing within the interface.

From this fact a high dislocation density at the

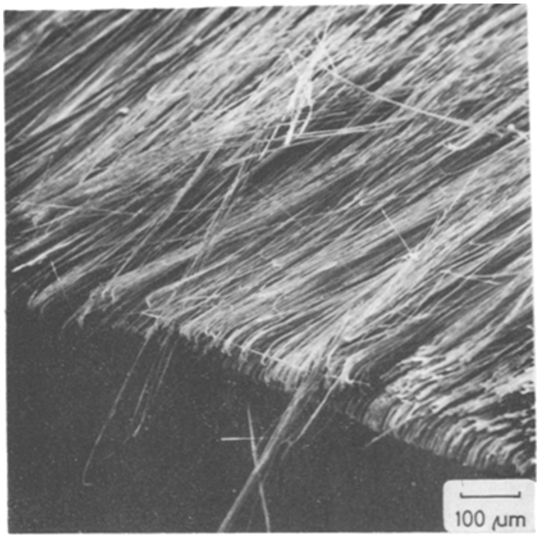

Figure 3 Scanning electron micrograph of deep-etched directionally solidified Ni_3Al–Mo alloy showing the infinite length of Mo fibres.

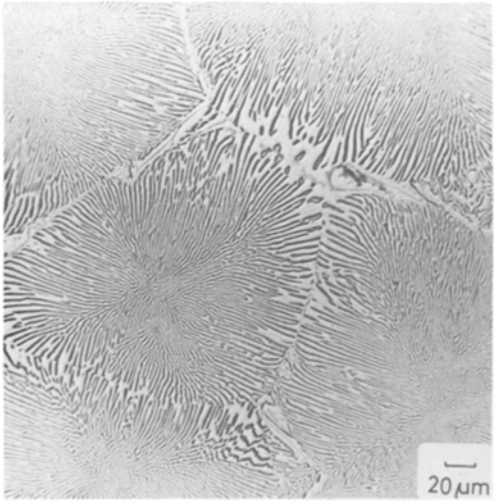

Figure 4 Formation of Mo blades during cellular growth at higher growth rates ($R = 18\ \mathrm{cm\,h^{-1}}$, transverse section).

interface can be deduced. Whether it has an influence on the mechanical properties of the aligned eutectic is a subject of further investigations.

At higher growth velocities, the observed cellular morphology is accompanied by a rod–blade transition of the Mo phase (Fig. 4). Since the two phases grow perpendicular to the curved solid–liquid interface, and the crystallographic orientation remains constant, this structural variation shows that bending of the Mo fibres due to the low energy of the solid–solid interface is not possible.

Alloys with compositions on the monovariant eutectic trough between γ'–α and γ–γ'–α could be grown in an aligned manner under the same conditions as the γ'–α pseudobinary eutectic. In these alloys, a third phase was present in the γ' matrix which could be indentified by SEM microanalysis as nickel with lower Al and higher Mo contents than $\gamma'(Ni_3Al)$. It was therefore concluded that this phase is γ(Ni) with precipitations of $\gamma'(Ni_3Al)$.

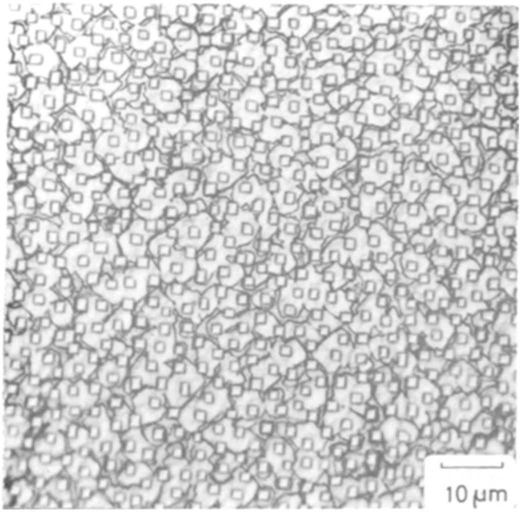

Figure 5 Transverse section of three phase γ'/γ–α alloy B ($Ni_{63.5}Mo_{21}Al_{15.5}$) showing regular distribution of the γ phase in the matrix.

A micrograph of an alloy of the composition $Ni_{63.5}Mo_{21}Al_{15.5}$ (alloy B of Fig. 1) is shown in Fig. 5. It is evident that the γ phase is not randomly distributed between γ' matrix and Mo fibres, as the γ'/γ interfaces are arranged mostly parallel to the diagonal of the Mo fibres' cross-section. Considering the determined relationship between γ' and α this would indicate an orientation of $(1\,1\,0)_{\gamma'} \parallel (1\,1\,0)_{\gamma}$ during growth. This unexpected result is in contrast to other γ–γ' containing ternary eutectics with Ni_3Nb or Ni_3Ta where no orientation relationship between the three phases could be observed.

It was anticipated that the direction of the monovariant trough strongly towards higher Mo contents (see Fig. 1) should result in a higher volume fraction of Mo fibres in the γ'–γ matrix. This was confirmed by comparing the volume percentages of Mo fibres of the investigated alloys A, B and C which were determined to be 18, 21 and

25 vol% Mo respectively. On the other hand, the volume ratio is also dependent on growth rate due to the decreasing solubility of γ and γ' for molybdenum with decreasing temperature. This indicates that the published value of 26 vol% Mo [4] for the pseudobinary alloy γ'–α is obviously based on a higher growth rate.

The interfibre spacing λ depends on the growth rate R according to the known relationship $\lambda^2 \cdot R$ = const. as found for almost all other known eutectic alloys. The value of $3 \times 10^{-11}\,\text{cm}^3\,\text{sec}^{-1}$ is of the same order as that observed for the NiAl–9 Mo eutectic [14] and almost constant for the compositions investigated.

The faceting of the Mo fibres indicates that only little or no coarsening should occur during annealing because the interface is constrained to lie in a low energy crystallographic plane [15]. This was verified by heating the alloys to 1100° C for 3 days. After this period, a change of microstructure could not be observed.

Hypereutectic alloys (Fig. 6) show Mo dendrites of quadratic cross-section, the direction of which obviously corresponds to the crystallographic relationship between the eutectic phases. Near the Mo dendrites the eutectic microstructure is not disturbed, which means that the primary growth tips should be located only a short distance before the eutectic crystallization front. This confirms the temperature measurements which show only small differences between liquidus and solidus for compositions outside the monovarient trough.

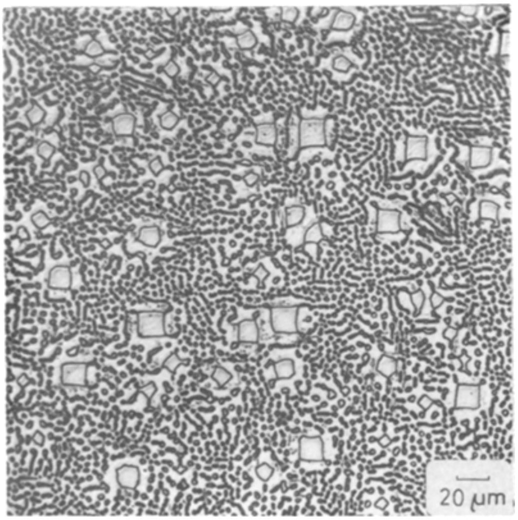

Figure 6 Transverse section of directionally solidified hypereutectic γ'/γ–α alloy C ($Ni_{61.6}Mo_{25.4}Al_{13}$) showing aligned primary Mo phase within γ'/γ–α eutectic.

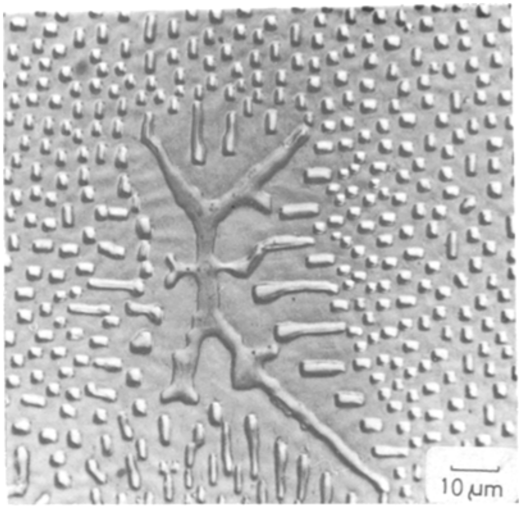

Figure 7 Transverse section of γ'/γ–α alloy with carbon impurities. Irregular-shaped phase is Mo_6Ni_6C.

In some cases an additional phase was present in the alloys, which is shown in Fig. 7. From X-ray powder diagrams it was concluded that this phase was a cubic η carbide with $a_0 = 10.89$ Å. By comparison with the literature data [16], a formula Mo_6Ni_6C is suggested. The formation of Mo lamellae near the η carbide dendrites indicates a deviation from plane front growth in these regions. The Mo_6Ni_6C phase is obviously formed from the melt, while in most Ni base alloys the η carbides are known to precipitate at grain boundaries [17].

The determination of the orientation relationship resulted in the observation that a crystallographic relation is also present between the matrix and the η carbides. The growth direction is parallel to $[1\,1\,0]_\eta$ and the interface between η and matrix is $(0\,0\,1)_\eta \parallel (1\,1\,0)_{\gamma',\gamma}$.

4.2. Properties

A few of the investigated alloys were characterized by their room temperature tensile behaviour. The tensile strength was found to be strongly dependent on the Mo content, varying from $940\,\text{MN}\,\text{m}^{-2}$ for the low Mo alloy to $1210\,\text{MN}\,\text{m}^{-2}$ for the high Mo alloy (growth rate in all cases $0.6\,\text{cm}\,\text{h}^{-1}$). The ductility is relatively high, i.e. 10 to 15% plastic strain for all samples. Examination of the fracture showed that deformation is confined to the region near the fracture surface. This behaviour is charac-

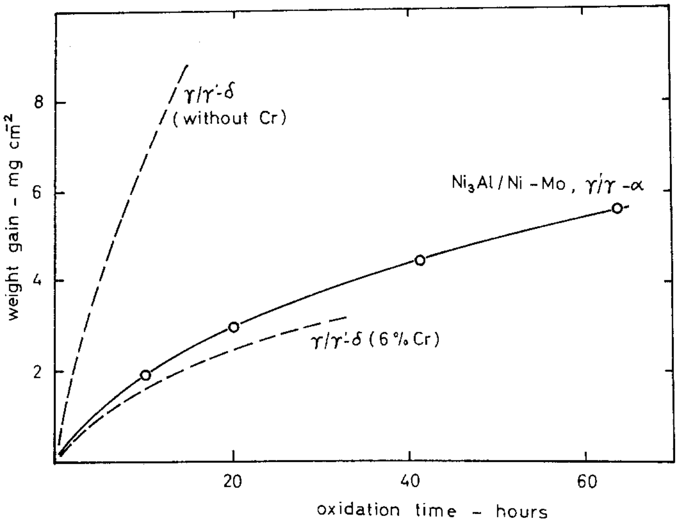

Figure 8 Oxidation behaviour of Ni–Mo–Al γ'/γ–α eutectic alloys under isothermal conditions at 1000° C in air.

teristic for a composite of a ductile matrix reinforced by ductile fibres.

Isothermal oxidation resistance was determined by weight-change measurements of a few samples at 1000° C in air. The results show a parabolic rate law weight-change data which are presented in Fig. 8. A remarkably low oxidation rate was observed which is of the same order as that of Ni/Ni_3Al–Ni_3Nb (γ/γ'–δ) alloys with 6% chromium.

X-ray powder photographs showed that the scale which partly spalled after cooling consisted mainly of NiO + $NiMoO_4$.

5. Conclusions

The results of the investigated Ni–Al–Mo alloys show that the proposed polythermal section Ni_3Al–Mo [9] is obviously not correct. The observed formation of pseudobinary γ'–α alloys from the melt suggests conversion of the peritectic formation of Ni_3Al in the Ni–Al binary system to a eutectic reaction between γ' and NiAl with additions of molybdenum. This property is a necessary condition for the existence of a maximum in the eutectic trough and a pseudobinary cut Ni_3Al–Mo.

The direction of this trough into the γ–γ'–α three-phase field suggests the possibility of fabricating composites with varying Mo fibre content. Room temperature measurements have confirmed that the strength increases with the volume fraction of Mo fibres.

It is anticipated that the properties of the ternary Ni–Mo–Al alloys may be improved by alloying. Chromium, in particular, should have a beneficial influence on the oxidation resistance as it is soluble in both matrix and fibres. Investigations in this field are the subject of current experiments.

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