# RECRYSTALLIZATION OF DISPERSION-HARDENED NICKEL ALLOYS WITH A POLYGONALIZED SUBSTRUCTURE

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UDC 669.018

The high heat resistance of dispersion-hardened nickel alloys is due to the presence of $ThO_2$, $HfO_2$, and other oxides, particles of which have been implanted in the matrix by a special technology. In addition to their inhibiting effect on the movement of dislocations at high temperatures [1], these hardener particles stabilize the structure and the substructure resulting from thermomechanical treatment of those alloys, in that they suppress recovery and recrystallization processes up to temperatures close to the melting point of the matrix [2-6]. Such an effectiveness of inclusions of a second phase, an effectiveness retained up to high temperatures, is made possible by the very slow coagulation of oxide particles according to the dissolution – precipitation mechanism [1, 7]. The degree of hardener dispersion may, however, also be changed by the coalescence of hardener particles at grain boundaries which move during either recovery or recrystallization [8-15], also during active elongation [16] or creep [8, 16, 17].

It is well known [9, 15, 18] that, in the general case, during the recrystallization of alloys containing macroscopic inclusions the boundaries may either move while "sweeping" the particles (if the moving force is too weak for tearing a boundary away from particles) or break away from the particles and thus the effect of the latter on the boundary migration process becomes negligible, while the boundaries of other grains remain stationary.

Inasmuch as substructure hardening is one effective and widely used methods of improving the heat resistance of dispersion-hardened alloys, it would seem very worthwhile to study the recrystallization of these alloys in the state where a substructure exists. Such a study has been made here on Ni–$ThO_2$ and Ni–$HfO_2$ alloys with various degrees of hardener dispersion and with a polygonized substructure resulting from thermomechanical treatment.

## EXPERIMENTAL METHOD

The processes of recovery and recrystallization during a high-temperature anneal in the structure of Ni–$ThO_2$ and Ni-$HfO_2$ alloys containing about 3% vol. oxides in various degrees of dispersion [19] were studied here by optical metallography and electron microscopy of foil and replica specimens, after they had been thermomechanically treated. Extruded alloy specimens were hot rolled and then recrystallization annealed at 1350°C for one hour resulting in a coarse-grain structure with grains about 0.5-1.0 mm in diameter. Both the fine-grain material (grain diameter about 1-5 μm) after hot rolling and the corase-grain material after recrystallization were subsequently subjected to several thermomechanical treatment cycles, each consisting of a cold roll to a 15% plastic deformation followed by an anneal at 1150°C for one hour. All alloys underwent ten such thermomechanical treatment cycles. The alloys with a coarse-grain structure were, in addition, also cold rolled to an 80% plastic deformation and then annealed at 1350°C for one hour.

These foils were produced by the method shown in [2]. Microsections for metallographical examination were obtained by mechanical grinding and subsequent electrolytic polishing. The coalescence of particles was studied in thin foils as well as in carbon-extraction replicas, the latter after their spray deposition on polished specimen surfaces at an about 45° angle to ensure self-shadowing. Such replicas were detached onto a water surface, after pre-etching with vapor of a 20% $HNO_3$ solution in ethyl alcohol. Thin foils and replicas were then examined under a model ÉVM-100L electron microscope. The size distribution of particles for plotting histo-

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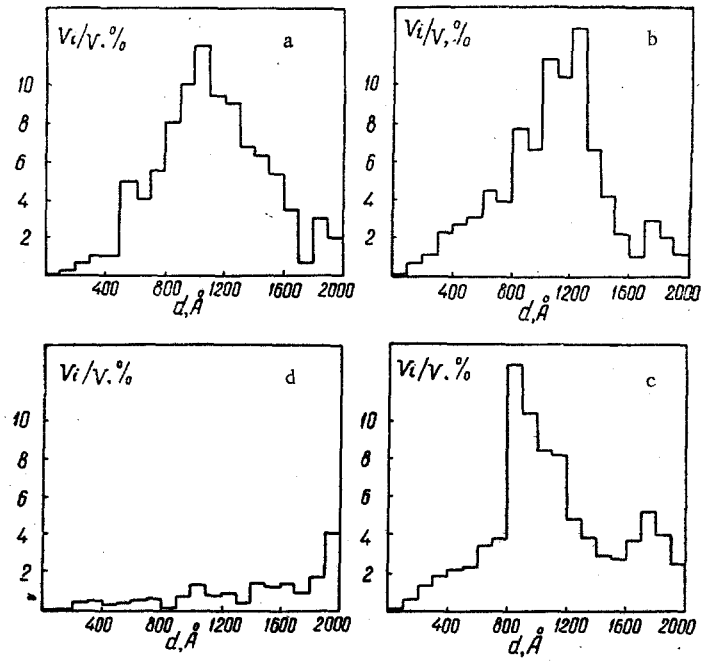


Fig. 1. Histograms representing the size distribution of particles in terms of volume fractions, in the following alloys: (a) $Ni-ThO_2$, (b) $Ni-HfO_2$ (I), (c) $Ni-HfO_2$ (II), (d) $Ni-HfO_2$ (III).

grams were determined in thin foils, over an area of approximately 100 $\mu m^2$ (about 5000 particles), just as had been done in [1]. High-temperature annealing was done with the specimens inside a nickel container under a vacuum of about $5 \cdot 10^{-5}$ torr.

Since in a dispersion-hardened alloy there may occur slow recrystallization (movement of boundaries together with particles, accompanied by the coalescence of the dispersoid at the boundaries) as well as fast recrystallization (movement of boundaries not significantly affected by particles), hence the mechanism of the process and the temperature at which slow recrystallization ($T_{sr}$) or fast recrystallization ($T_{fr}$) begins can be established only by a composite use of all the three methods. As the temperature of the beginning of recrystallization in our study we regarded the temperature at which, after one hour of annealing, recrystallization nuclei of microscopic size in the alloy structure could be revealed only under an electron microscope.

## RESULTS

Histograms representing the size distribution of particles in terms of volume fractions in $Ni-ThO_2$ and $Ni-HfO_2$ alloys (I, II, III) with various dispersion levels of $HfO_2$ particles have been plotted in Fig. 1. With the values of volume fractions $V_i$ of particles of radii $r_i$ according to this histogram, one can calculate the mean interparticle distance R according to the formula [20]

$$R^2 = \frac{8}{3\Sigma V_i/r_i^2}.$$

The volume fraction of particles within a given range can also be determined from this histogram. The ratio between the number of coarse particles and fine particles in an alloy is characterized by the average diameter $\bar{d}$. According to the data in Table 1, the $Ni-ThO_2$ alloy contains particles of the largest average size and, at the same time, distance R is the shortest here and particles within the 500-1500 Å range take up the largest volume fraction.

After repeated thermomechanical treatment, there forms in all alloys a polygonal substructure with a block size depending on the dispersion level of particles and corresponding to the mean interparticle distance in the alloy (Table 1). It must be pointed out that, although in alloy III the distance R between particles with a diameter d > 500 Å is large, the diameter of subgrains forming here is equal to only half this distance. Since a polygonal substructure forms on particles with a diameter d > 500 Å and in a developed block structure such

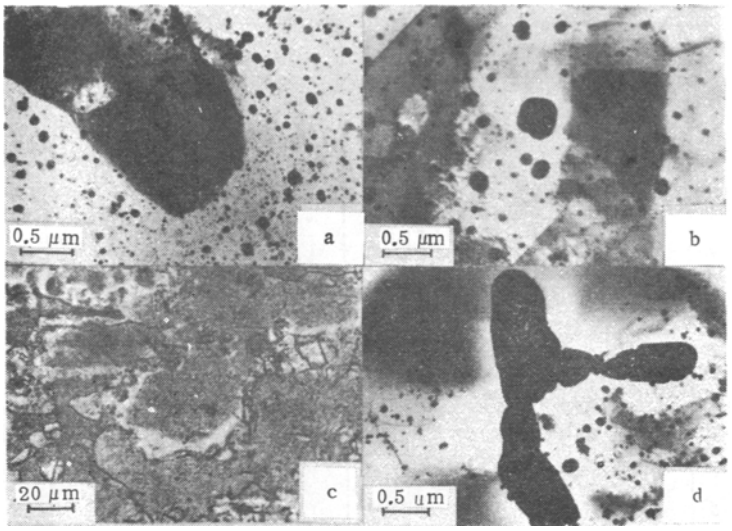


Fig. 2. Microstructure of Ni−$HfO_2$ alloys after high-temperature annealing: (a), (b) Ni−$HfO_2$ (I) at T = 1400°C for one hour, (c) Ni−$HfO_2$ (I) at T = 1420°C for one hour, (d) Ni−$HfO_2$ (II) at T = 1400°C for one hour.

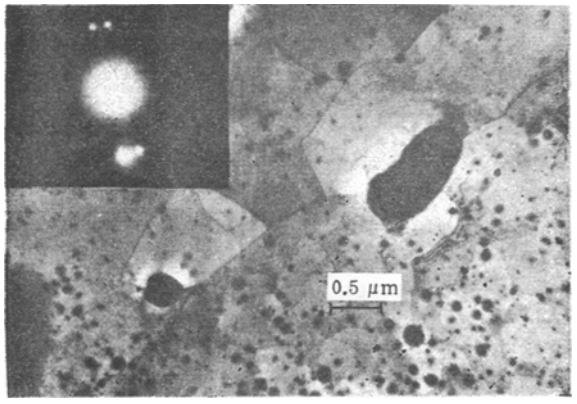


Fig. 3. Movement of a subboundary with an aximuthal disorientation within $\theta \sim 10°$, with a "sweep" of particles, in Ni−$HfO_2$ (II) annealed at 1400°C for one hour.

particles exist at the junctions between subboundaries [2], hence in Ni−$ThO_2$ and alloys I, II most of these junctions are free of particles with a diameter d > 500 Å and, therefore, fine particles may effectively plug the subboundaries, if only because their diameter is likely to be smaller than the mean distance between dislocations along a subboundary [18]. While such an alloy undergoes annealing, subgrains may grow fast and recrystallization nuclei may form due, for instance, to a shift of the "triple point" [21]. Indeed, the temperature at which fast recrystallization begins ($T_{fr}$) is the lowest for alloy III. For alloys I and II we find that $T_{fr} = T_{sr} = T_r$. This temperature ($T_r$) is higher for alloy I than for alloy II and, moreover, the structures of these two alloys after annealing at $T_r$ are very different. While in alloy I after annealing at $T_r$ = 1400°C for one hour most of the volume has been recrystallized by the fast mechanism (Fig. 2a) and regions with coalescence of particles are extremely sparse (Fig. 2b), the opposite takes place in alloy II, namely after annealing at $T_r$ = 1360°C for one hour its structure becomes transformed by the slow recrystallization mechanism and regions of fast anomalous crystal growth are very few. An additional anneal of alloys I and II for one hour at 1420°C and 1400°C, respectively, produces a movement of boundaries with a "sweep" of particles in the grains which have grown during fast recrystallization. Simultaneously, within the unrecrystallized regions there emerge new grains whose growth is accompanied by a coalescence of particles at the boundaries (Fig. 2c). These processes are particularly intensive in alloy II, displace agglomerates a few microns large (Fig. 2d).

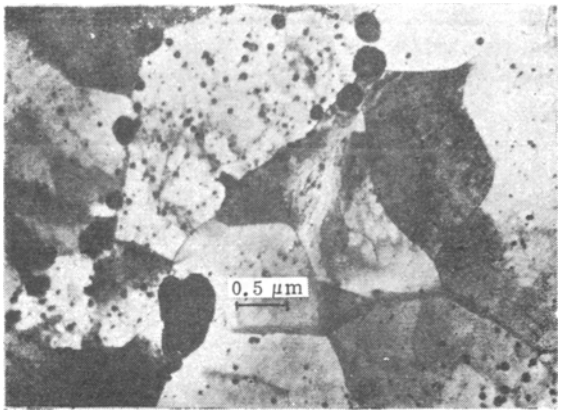


Fig. 4. Breakup of a cluster of subgrains, with a formation of agglomerates of particles, in Ni–$HfO_2$ alloy II annealed at 1400°C for one hour.

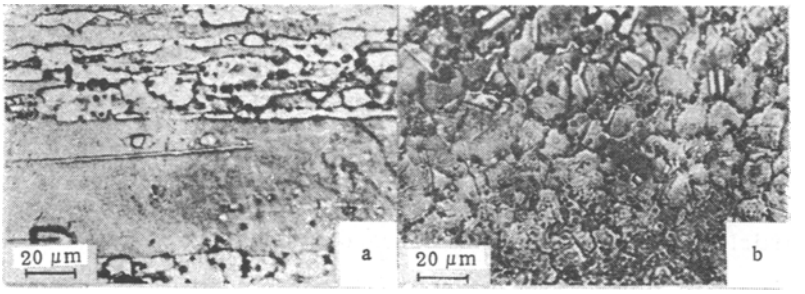


Fig. 5. Nucleation and growth of new grains in (a) the coarse-grain structure and (b) the fine-grain structure of Ni–$HfO_2$ alloy (II) annealed at 1420°C for one hour.

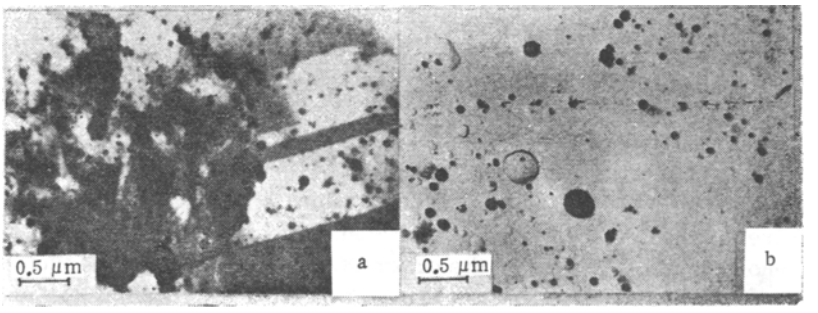


Fig. 6. Coalescence of particles at moving boundaries: (a) Ni–$HfO_2$ (I) annealed at T = 1350°C for one hour after deformation to $\varepsilon \sim 80\%$, (b) Ni–$ThO_2$ annealed at $T \sim T_{melt}$ for one hour after repeated thermomechanical treatment.

In the course of examining the structures where slow recrystallization had occurred, we detected small-angle block boundaries with a rather high degree of disorientation and moving with a "sweep" of particles (Fig. 3). Particles "swept" from the matrix, as in the case of a wide-angle boundary, have coalesced at subboundaries. It is noteworthy that within the region behind a moving boundary (Fig. 4) or subboundary (Fig. 3), where hardly any dispersoid can be found, the substructure does not vanish completely but only becomes coarser. The disorientation of subgrains within these regions remains within approximately 1°, as measured with a goniometer. Such regions often surround partly coalescing agglomerates of dispersoid particles (Fig. 4). One may assume that in such cases clusters of subgrains have been "broken up." An analogous phenomenon, but during agglomerative recrystallization, had been observed in dispersion-hardened copper [13].

TABLE 1

| Alloy | $R$, Å | $R$, Å $d > 500$ | $V$, % 500—1500 | $\bar{d}$, Å | $\bar{D}$, Å | $f_p^0$ | $f_p^{500-1500}$ | $T_{fr}$, °C | $T_{sr}$, °C |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $10^6$, dyn/cm$^2$ | | | |
| Ni—$ThO_2$ | 3610 | 4800 | 2,46 | 364 | 3000 | 9,0 | 8,0 | 1420 | $\sim T_{nl}$ |
| Ni—$HfO_2$ (I) | 3800 | 5800 | 2,40 | 320 | 4700 | 8,9 | 7,0 | 1400 | 1400 |
| Ni—$HfO_2$ (II) | 3830 | 6600 | 2,12 | 216 | 5000 | 8,7 | 6,2 | 1360 | 1360 |
| Ni—$HfO_2$ (III) | 6380 | 11500 | 0,24 | 231 | 6000 | 0,8 | 0,5 | 1300 | — |

This study concerning the nucleation and the growth of new grains during slow recrystallization in alloy II at 1420°C has revealed that the nucleation process occurs near the boundaries of old grains. This is why, after repeated thermomechanical treatment, the chains of new grains appear elongated in the direction of rolling in the coarse-grain alloy and distributed almost uniformly in the fine-grain alloy (Fig. 5).

An anneal of all these alloys at 1350° for one hour, after cold rolling to a high degree of deformation (about 80%), is accompanied by an intensifying process of fast recrystallization. In Ni—$HfO_2$ (I, II) alloys, however, at the boundaries between recrystallized and unrecrystallized regions there can sometimes begin the initial stage of coalescence of particles (Fig. 6a), which indicates a transition from fast to slow recrystallization. We will note here that no symptoms of slow recrystallization were observed in the Ni—$ThO_2$ alloy under these conditions in our study, while coalescence of particles at a moving boundary was found only within the polygonal substructure near the melting zone (Fig. 6b).

## DISCUSSION OF RESULTS

A movement of particles together with grain boundaries (slow recrystallization) is possible only when [22]

$$f_p \geqslant f_d, \tag{1}$$

where force $f_p$ is the resistance of particles to a movement of a boundary and the driving force $f_d$ moves a boundary, the latter force being associated with the decrease in free energy ($\Delta F$) during such a boundary movement. Using the analogy between the process of substructure coarsening and the process of agglomerative recrystallization in a block structure [23], we can calculate the driving force in this process according to the expression [24]

$$f_d = \Delta F = \frac{2\sigma_s}{\bar{D}}, \tag{2}$$

where $\bar{D}$ is the average diameter of structural blocks and $\sigma_s$ is the surface energy of subboundaries. The energy of wide-angle boundaries in the Ni—$ThO_2$ alloy is known from the experiment in [25] ($\sigma_B \approx 1080$ ergs/cm$^2$). It has been established already that most blocks in a polygonal substructure of the alloys in this study are disoriented relative to one another within angles of the order of a few degrees [2]. Assuming the average disorientation angle to be $\theta \approx 4°$, we can calculate the energy of subgrains according to the expression in [26] rewritten (with $\sigma_{max} = \sigma_B$)

$$\frac{\sigma_s}{\sigma_B} = \frac{\theta_s}{\theta_{max}}\left[1 - \ln\frac{\theta_s}{\theta_{max}}\right], \tag{3}$$

where $\sigma_{max}$ is the energy of a subboundary with a disorientation angle $\theta_{max} \approx 25°$ [26] and $\sigma_B$ is the surface energy of a grain boundary. Inserting the value $\sigma_s \approx 490$ ergs/cm$^2$ calculated according to (3) and the value $D = 0.48 \cdot 10^{-4}$ cm (from Table 1) into expression (2), we obtain $\Delta F \approx 2 \cdot 10^7$ ergs/cm$^3$. The resistance force of particles in these alloys will be calculated according to the expression [27]

$$f_p = \frac{3\sigma V}{2r}, \tag{4}$$

where $\sigma$ is the energy of a moving boundary or subboundary, V is the volume fraction of particles of the second phase, and r is the radius of particles. For the alloys in this study, with a wide size-distribution spectrum of particles, this expression may be rewritten as

$$f_p = 3\sigma \sum_i \frac{V_i}{2r_i}, \tag{4a}$$

where $V_i$ is the volume fraction of particles with the radius $r_i$. Calculated values of the resistance force, of particles within the 500-1500 Å size range $f_p^{500-1500}$, and of all particles $f_p^0$ are given in Table 1. The data here indicate that particles within the 500-1500 Å size range contribute most to the resistance to boundary movement in the given alloys. In $Ni-ThO_2$ and alloys I, II the resistance force and the driving force during recrystallization in a block structure are of the same order of magnitude, i.e., condition (1) is satisfied and the simultaneous movement of particles and boundaries in our experiment is thus explained. In alloy III, evidently, particles do not significantly affect the recrystallization process in a polygonized substructure, inasmuch as the driving force of recrystallization exceeds the resistance force by more than one order of magnitude. In the case of recrystallization in a highly deformed structure ($\varepsilon \approx 80\%$) we have a driving force $\Delta F \approx \rho G b^2 \approx 10^9$ ergs/cm$^3$ ($\rho \simeq 10^{12}$ cm$^{-2}$, $b \simeq 2.5 \cdot 10^{-8}$ cm, $G \simeq 2.1 \cdot 10^{12}$ dyn/cm$^2$) almost two orders of magnitude larger than the resistance force and, therefore, fast recrystallization takes place in all alloys during annealing. Some boundary movement together with particles into a deformed region of the structure is, evidently, the result of recovery and polygonization processes which occur ahead of the front of the moving boundary and which lower appreciably the stored energy as well as, along with it, the driving force of boundary movement. The different behavior of $Ni-ThO_2$ and $Ni-HfO_2$ (I, II) alloys may be attributed to the different degrees of hardener dispersion. Although this difference in the dispersion of hardener particles does not make a great difference in the resisting force $f_p$, but even a small increase in the force $f_p$ may, evidently, significantly affect the beginning of boundary movement with a "sweep" of particles when $f_p$ and $f_d$ are of nearly the same magnitude. Since the beginning of boundary movement with a "sweep" of particles brings about a coalescence of particles at the boundaries, hence it is possible that this process will increase the driving force of boundary movement, inasmuch as this process is accompanied by a decrease in free energy during the coarsening of particles. Therefore, the increase in force $f_p$ due to accumulation of particles at a boundary may be compensated by an increase in force $f_d$ so that condition (1) will still be satisfied.

The mechanism of fast recrystallization prevails in $Ni-ThO_2$ and $Ni-HfO_2$ (I) alloys at $T = T_r$, while the mechanism of slow recrystallization prevails in alloy II. The intensification of fast recrystallization in those two alloys may be a consequence of a much higher energy stored in the system with large volume fraction of coarser particles, because we know that during deformation the diameter of the plastic region around a particle remains proportional to the diameter of this particle [28] and during annealing the coarse particles retain a larger number of dislocations [2]. Furthermore, also the diameter of subgrains after repeated thermomechanical treatment depends on the relative volume fraction of particles within the 500-1500 Å size range [2] and with a decrease in this diameter there increases the stored energy. Therefore, in $Ni-ThO_2$ and $Ni-HfO_2$ (I) alloys at $T = T_r$ there takes place, essentially, fast recrystallization, during which the substructural hardening vanishes, i.e., the potential sites disappear where movement of subboundaries with a "sweep" of dispersoid particles and coalescence of the latter could begin. According to this interpretation, fast and slow recrystallization in dispersion-hardened alloys are two competing processes.

The nucleation of new grains near original grain boundaries in a block structure, as revealed in our study, may be a different result than that of the matrix concentration of elements which increase the mobility of oxide particles in the nickel matrix. Such an effect of harmful impurities, causing an appreciable lowering of the recrystallization temperature and an agglomeration of particles, was also noted in earlier studies [29, 30]. The mobility of oxide particles in the metallic phase may, for instance, be increased by a change in the concentration of oxygen [31] which can diffuse here from the furnace atmosphere.

The intensive coalescence of particles at moving boundaries occurs, evidently, as a result of collisions between particles and the thus-established interphase contact with an accompanying fast sinter by the self-diffusion mechanism [32]. Collision between particles during boundary movement can take place in two ways. First, particles moving together with a boundary collide with particles situated in the matrix; secondly, the elimination of local segments with a small curvature from a moving boundary may bring particles closer together. This process is a very likely one, inasmuch as the driving force which decreases the curvature and which can be calculated according to the expression [27]

$$\Delta F = \frac{2\sigma_B}{r_\kappa} \approx \frac{2\sigma_B}{R} \approx 4.5 \cdot 10^7 \text{ ergs/cm}^3$$

($r_k$ is the local radius of curvature, assumed equal to the mean distance between particles) is of the same order of magnitude as the driving force which moves grain boundaries in a polygonal substructure of our alloys. No evidence has been found to indicate the role of diffusion of the material of particles along grain boundaries during coalescence of these particles.

## CONCLUSIONS

1. High-temperature annealing of dispersion-hardened nickel alloys, with a substructure specially polygonized by thermomechanical treatment, is accompanied by two competing processes: fast and slow recrystallization. The latter leads to a coalescence of hardener particles at moving boundaries.

2. Both recrystallization processes are sensitive to changes in the dispersion level of hardener particles, within a rather narrow range of this variation. In dispersion-hardened nickel alloys there occurs a regular lowering of the recrystallization temperature and a transition from fast to slow recrystallization, all related to a decrease in the volume fraction of particles within the 500-1500 Å size range.

3. An appreciable change in the degree of hardener dispersion in $Ni-HfO_2$ (III), along with lowering of the recrystallization temperature, will accelerate the process of fast recrystallization.

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