

설파민산 니켈 도금욕에서의 니켈 전착

Electrodeposition of Nickel from Nickel Sulphamate Baths*

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Abstract

About 1 mm thick nickel electrodeposits were obtained from nickel sulphamate baths at 40 to 60°C over the range of current densities from 5 to 25 A/dm². Deposits from above about 1.2V of cathode overpotential had randomly distributed fine grains due to a higher nucleation rate and hence had a high hardness. A deposit obtained at 0.63 V had the [110] orientation with a field oriented fine structure which yield a relatively high hardness. Deposite obtained at the intermediate overpotentials showed the [100] orientation with coarse field oriented structure whose column width tended to decrease with increasing cathode overpotential, which, in turn, gave rise to an increase in hardness. Residual stresses of the deposits measured by X-ray technique were mostly tensile but did not exceed 80 MPa, and were occasionally very small compressive. The cathode current efficiency was above 90% in all the electrolysis conditions, whereas the anode current efficiency varied from 50 to 90% with current density, bath temperature and nickel chloride concentration, among which the chloride was the most influential.

〈요 지〉

설파민산 니켈 용액으로 40~60°C 온도와 5~25A/dm²의 전류밀도 범위에서 1mm 두께까지 니켈을 전착시켰다. 1.2V 이상의 음극 과전압 크기에서 핵발생 속도의 증가에 따라 미세한 결정립 크기의 무질서 방위가 나타났고 0.63V에서 미세한(110) 우선 방위가 나타났으며 그 사이의 크기에서는 강한(100) 우선방위가 형성되었다. (100) 우선방위는 조대한 주상정 조직을 나타냈고, 그 주상정의 폭은 전류밀도가 증가하면 감소하였다. X-ray응력 측정장치로 측정된 전착층 표면의 잔류응력 크기는 대부분 인장응력으로써 80MPa 이내였고 가끔 매우 작은 압축응력도 나타났다. 음극의 전류효율은 90% 이상이었으나 양극의 효율은 전류밀도, 온도, 특히 염화니켈의 양에 따라 50~90%의 효율을 나타냈다.

1. INTRODUCTION

The structure and orientation of electrodeposited nickel are affected by the conditions of electrolysis(1-4). Lee et al. (5) suggested

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that the preferred orientation of metal deposits was associated with both the cathode overpotential and the surface energy of lattice planes in the deposit crystals and that the texture of copper deposits should develop in the order [110], [100] and [111] with increasing cathode overpotential for fcc crystals. The concept was found to be applied to other deposits of chromium (6) and nickel (1-3). The microstructure of cross sections of deposit was related to its preferred orientation (1-3,5,6) unless electrodeposition was influenced by any cyclic disturbances and organic agents (3). In this study, cathode overpotential, texture, microstructure, residual stress and hardness of deposits from nickel sulfamate solutions, which are particularly useful to thick electrodeposition, were measured and their mutual relationships were examined.

2. EXPERIMENTAL PROCEDURE

Four types of nickel sulfamate solutions were used in this study (Table 1). A 1 mm thick copper sheet was polished with an emery paper, degreased in an alkali solution composed of 12g/l caustic soda, 11g/l sodium carbonate, 18g/l Na_2SiO_3 and 19g/l $\text{CH}_3(\text{CH})_{11}\text{SO}_3\text{Na}$ for 10 minutes, and then electropolished in a phosphoric acid solution ($\text{H}_3\text{PO}_4 : \text{H}_2\text{O} = 1:1$). The polished sheet was used as a cathode after insertion into teflon case that confined electrodeposition to a circular area of 16mm diameter. A nickel sheet of 99.9% in purity was dipped in a dilute sulphuric acid solution to dissolve oxide scale, degreased in an alkali

Table 1. Composition of plating baths (g/l).

compound	D	B	K	L
Ni $(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$	300	450	600	600
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	6	0	5	3
H_3BO_3	30	30	40	30
$\text{CH}_3(\text{CH})_{11}\text{SO}_3\text{Na}$	0.7	0.7	0.7	0.7

solution and used as an anode after insertion into the teflon case. The distance between the anode and cathode was about 30mm. Current density ranged from 5 to 25 A/dm^2 in a stirred bath. Temperature ranged from 40 to 60°C and was regulated within $\pm 1^\circ\text{C}$. Deposit thickness was about 1 mm.

To avoid fluctuations of bath compositions, under any circumstances bath solutions were used no more than one time and frequently checked by atomic absorption analyzer.

The cathode overpotential, which is defined as measured cathode potential minus equilibrium cathode potential, was measured under various conditions of electrolysis using a potentiometer. Electrodeposited specimens were subjected to X-ray diffraction to determine the preferred orientation and the residual stress or internal stress (7). The orientation of the deposit was expressed in terms of a texture coefficient, TC, which is defined as follows:

$$\text{TC} = \frac{I(\text{hkl}) I_0(\text{hkl})}{(1/n) \sum \{I(\text{hkl}) / I_0(\text{hkl})\}}$$

where $I(\text{hkl})$ and $I_0(\text{hkl})$ are the integrated intensities of (hkl) reflections measured for an experimental specimen and a standard powder sample, respectively and n is the total number of reflection planes. When the TC of all reflection planes is unity, the distribution of crystal orientation is random. When the TC of any (hkl) plane is larger than unity, a preferred orientation exists in which grains are oriented with their (hkl) planes parallel to the surface. The larger the value of TC, the greater the degree of preferred orientation. In this study, (111), (200), (220), (311), (222), (400), (331) and (420) reflections were measured. TC's of (111) and (222) planes, or TC's of (200) and (400) planes should be same, but they are hardly same because of errors in in-

tensity measurements. In this case average TC may be used.

After examination of X-ray diffraction, cross sections of the specimens were polished and etched in a solution of 10ml distilled water, 50ml nitric and 50ml glacial acetic acid for 2 minutes and observed under a metallurgical microscope. The surfaces of deposits were examined using a transmission electron microscope after they were ground by 0.3 mm from inner surface 0.1 mm from outer surface, thinned to 50 μm in a mixture of 30 ml nitric acid, 10ml sulfuric acid, 10ml phosphoric acid and 50ml glacial acetic acid, and further electropolished in a solution of 860g/l phosphoric acid, 50g/l sulphuric acid and 10g/l chromic acid. Copper substrate of the deposit was earlier removed by dissolving in a solution of 500 g/l CrO_3 and 50g/l sulfuric acid. The Vickers hardness test of the nickel deposits was made at the load of 250 g.

3. RESULTS AND DISCUSSION

3.1. Cathode Overpotential and Current Efficiency

Figure 1 shows variations of cathode overpotential with temperature and current density in the baths. The cathode overpotential increased with increasing current density and decreasing bath temperature as usual. The large change in overpotential with current density and temperature for the bath B seems to be due to an absence of chlorine ion. It also appears that the overpotential increases with decreasing chlorine ion. The cathode current efficiency was over 90% in all the baths, whereas the anode current efficiency varied from 50 to 90% with bath temperature, current density and type of bath. The anode current efficiency

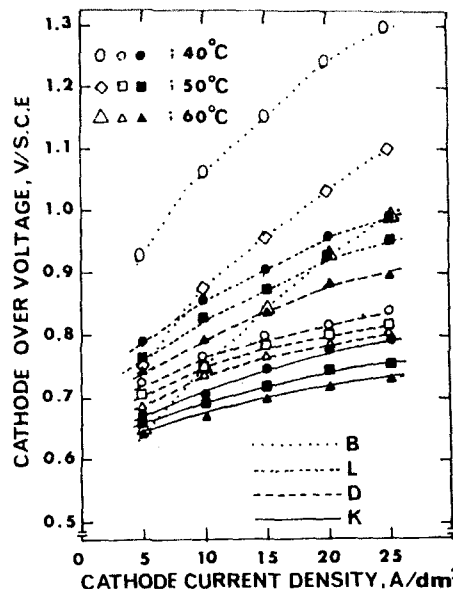


Fig. 1. Cathode overvoltage vs. cathode current density at various bath temperatures.

increased with increasing bath temperature and decreasing current density as usual. The anode current efficiency in bath B was lowest among the four types of baths, and that was attributed to absence of chloride ion which is known as an efficient corroding element.

3.2. Residual Stress

Figure 2 shows residual stresses or internal stresses of the deposits were mostly tensile, whose magnitudes did not exceed 80MPa, and were occasionally a little compressive. The stresses were insensitive to current density at bath temperatures of 40 and 50°C, whereas they were in minima at 10 to 15 A/dm² when the bath temperature was 60°C. In general the bath temperature of 50°C yielded the minimum residual stresses. The stresses of the specimens from baths L and B were lower possibly due to the lower chlorine ion concentration. Any-how the low residual stresses are very

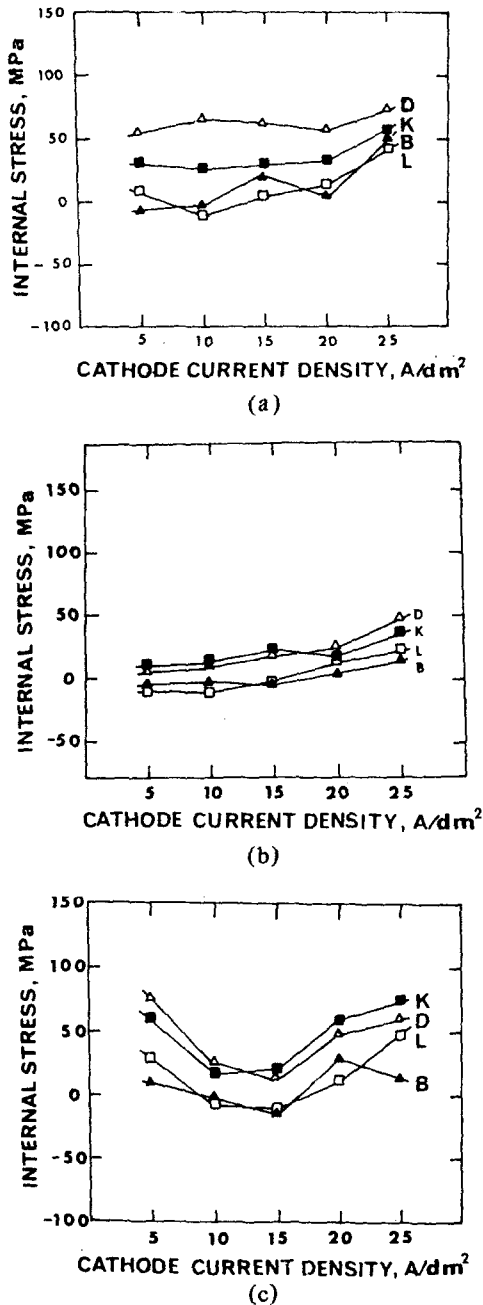
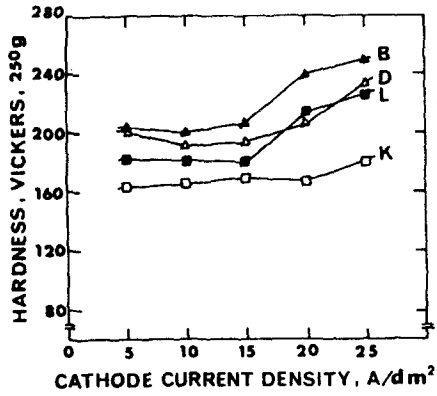


Fig. 2. Residual stress in electrodeposits from four solutions at (1) 40, (b) 50 and (c) 60°C as a function of cathode current density.

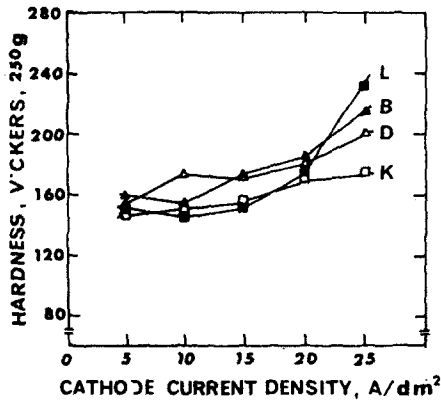
encouraging in a thick electrodeposition. Otherwise the deposits tend to crack or to peel off from the substrates. A problem in measuring residual stresses was that the specimens were assumed to behave isotropically in contrast with experimental data showing strong texture development in them. However, for lack of any strong correspondence between texture and residual stress, most specimens having similar textures, the present data could be sufficiently useful for the purpose of comparison.

3.3. Hardness

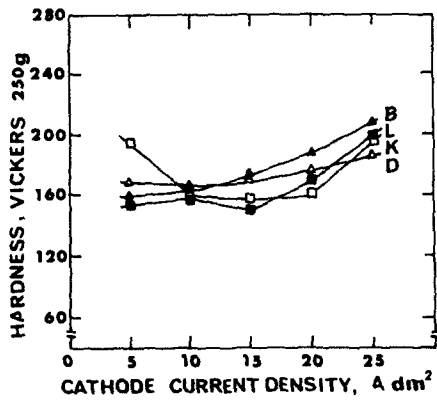
The results of hardness test are shown in Fig. 3. The hardness of the deposits increased with increasing current density and decreasing bath temperature as usual. The increase in the current density and the decrease in the bath temperature tend to increase the nucleation rate and hence give rise to finer grain sizes, which, in turn, yield the higher hardness (Fig. 4). A strong deviation from the trend is noted in the specimen from solution K at 60°C and 5 A/dm² (Fig. 3C) which had a relatively fine structure due to the [110] texture (see Microstructure). As the current density increased and the bath temperature decreased, the cathod overpotential tended to increase. Therefore the hardness may be related to the overpotential. Figure 5 shows the hardness as a function of the cathode overpotential. For a given type of solution, the hardness increased with increasing overvoltage. For a given cathode overpotential the higher chloride ion tended to yield the higher hardness. It is interesting to note that data from solutions D and K which had similar chloride ion concentrations are on a narrow band.



(a)

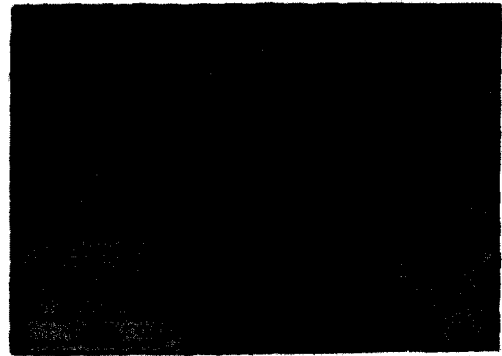


(b)



(c)

Fig. 3. Microhardness in electrodeposits from four solutions at (a) 40, (b) 50 and (c) 60°C vs. cathode current density.



(a)



(b)

Fig. 4. Transmission electron micrographs of deposits from solution K at 40°C. (a) Current density = 5A/dm²; (b) 25 A/dm².

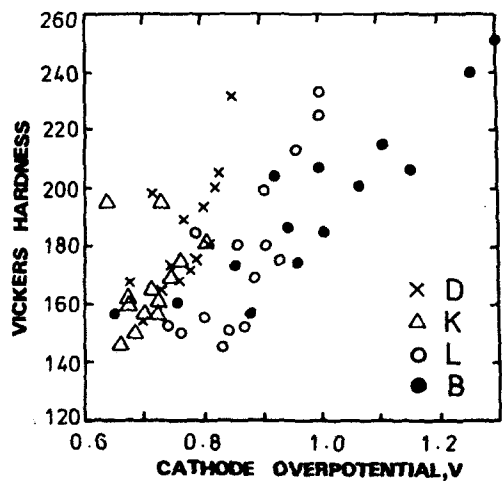


Fig. 5. Hardness vs. cathode overpotential.

3.4. Preferred Orientation

The texture coefficient of the reflection planes of nickel electrodeposits obtained under various conditions of electrolysis are plotted as a function of cathode overpotential in Fig. 6. The reflection planes whose textures were far less than unity are not shown in the figure. Most specimens, in which the texture coefficients of (100) plane were larger than 1, had [100] texture. One specimen from the cathode overpotential of 0.63 V, which was the lowest potential in this study, had [110] texture. At the cathode overpotentials above about 1.1 V, the texture coefficients of various planes approach unity, except one specimen from 1.25 V having strong (120) reflection which might be caused by measured error, indicating a random distribution of crystals. The results are generally in agreement with earlier results from dull nickel, Watts and bright nickel electrodeposits (1-3). Therefore the same explanation can be applied to the present results.

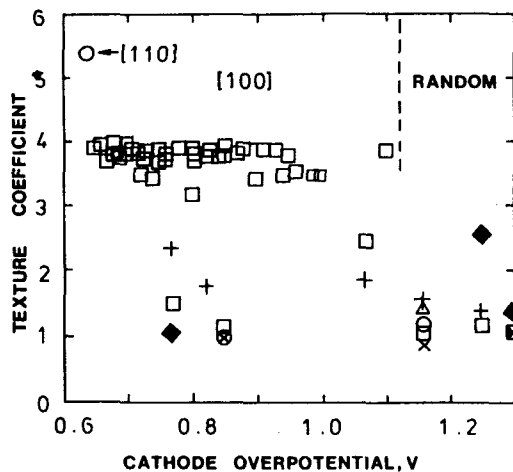


Fig. 6. Texture coefficient of \circ (110), \square (100), \times (111), $+$ (311) and \blacklozenge (210) planes vs. cathode overpotential.

Figure 7 shows a two-dimensional model of two adjacent crystals. The surface energy of a crystal facet parallel to plane CD of grain A is larger than that of grain B, that is, crystal A has a higher ledge density than crystal B ($\alpha > \beta$). Planes parallel to plane CE must be the most closely packed planes which have the minimum surface energy. Arrows indicate impinging ions. Squares attached to the surface of crystals indicate newly deposited atoms. Atoms are not always deposited directly to ledges. Atoms deposited on flat surface (M in Fig. 7a) are in a less stable state than atoms at ledges, because they are less bonded than atoms at ledges. Therefore they diffuse to ledges. If the cathode polarization is low (i.e., low cathode overvoltage), the ion concentration next to the deposit will high. This situation may be depicted schematically as shown in Fig. 7 (a). In this case crystal B is expected to have more atoms deposited on between ledges than crystal A, because the average diffusion distance on crystal A is shorter than on crystal

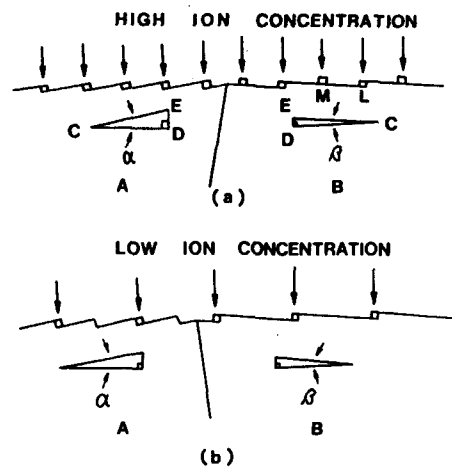


Fig. 7. A two-dimensional model leading to a preferred orientation.

B. Therefore the configuration on crystal A is more stable than on crystal B, resulting in the growth of crystal A at the expense of crystal B. In this case the deposit will assume the orientation of crystal A which has the higher surface energy plane normal to the direction of deposit growth. If the polarization is raised, the ion concentration next to the deposit will be decreased. The situation may be shown in Fig. 7(b). In this case the surface area to be covered by deposited atoms is larger for crystal A than for crystal B, because angle α is larger than angle β . Therefore crystal B will grow at the expense of crystal A. Thus the deposit will assume the orientation of crystal B. It should be noted that the shorter diffusion distance to ledges on crystal A cannot make crystal growth faster as in the case of low polarization, because ions are not sufficiently supplied. At sufficiently high polarization, impinging ions crystallize almost as soon as they arrive at the surface and the crystallites cannot grow extensively and therefore a preferred orientation does not develop. The deposit will consist of very fine grains with nearly random orientation. It follows from the above discussion that the orientation of fcc crystals will change from the [110] texture to the [111] texture passing through the [100] texture, since $\gamma(110) < \gamma(100) < \gamma(111)$ where $\gamma(111)$ is surface energy of (111) plane, and finally to the random orientation with increasing cathode polarization or overpotential. Our results showing the development of [110] orientation at the low cathode overpotential of 0.64 V and the formation of [100] orientation in the intermediate range of 0.63 to 1.1 V are compatible with the preceding explanation. In the higher range of overpotential a random distribution of crystals developed

without [111] texture region. We cannot always obtain all textures in possible electrolysis conditions. In an electrodeposition of copper, where the [110], [100] and [111] textures were obtained, the texture sequence was compatible with the above explanation (5).

3.5. Microstructure

Lee et al. (1-3,5,6) found that the microstructures of cross sections of electrodeposits were closely correlated with preferred orientation. Figure 8(a) shows a microstructure of the deposit (Sol. K, 60°C, 5A/dm²) with [110] texture which is characterized by a fine field oriented structure. Figure 8(b) shows a microstructure of the deposit (sol. B, 60°C, 5A/dm²) with [100] texture which is characterized by a coarse field oriented structure whose columns are frequently crossed by a slant twins. Figure 8(c) shows a microstructure of the deposit (Sol. B, 40°C, 25A/dm²) with random distribution of crystals which is characterized by an unoriented dispersion type of texture. Interplanar angles in cubic crystals between planes of [111] and [110] are 35.3° and 90°. Grains tend to grow along the direction of electric field. When [110] directions are parallel to the field direction (e.e., [110] texture), [111] planes are parallel to the field directions. Therefore the lowest surface energy plane [111] become boundaries of elongated grains. Since the grain boundaries have low energy, diameter of the grains can be small and fine field oriented grains can develop in the electrodeposits. On the other hand, interplanar angle between planes of [111] and [100] is 54.7°. Therefore grains of a deposit with [100] texture are expected to have higher grain boundary energy parallel to the field direction, resulting

in coarse columnar grains, which have slant twins, because [111] are twin planes. At the high cathode overpotential, the nucleation rate is very high and the deposit is expected to have randomly distributed fine grains.

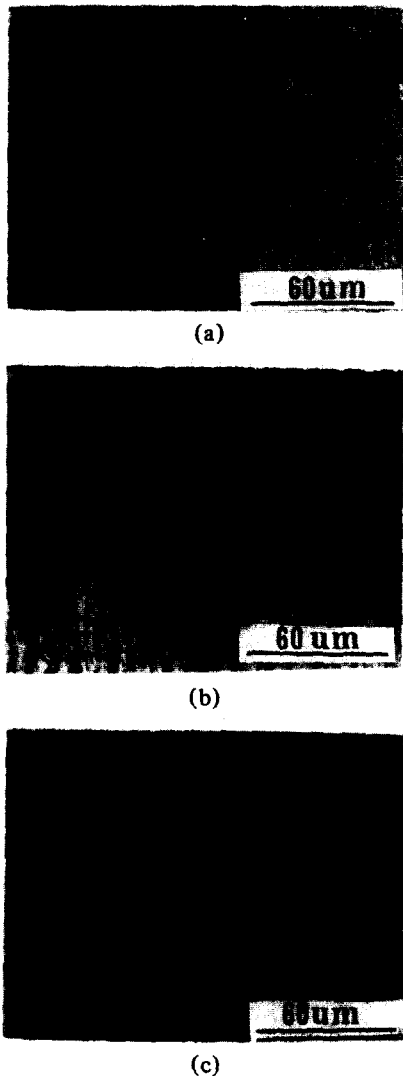


Fig. 8. MICROSTRUCTURES OF CROSS SECTIONS OF DEPOSITS WITH (a) [110], (b) [100] and (c) RANDOM ORIENTATIONS

4. CONCLUSION

About 1 mm thick nickel electrodeposits were obtained from four types of nickel sulfamate baths at temperatures from 40 to 60°C over the range of current densities from 5 to 25 A/dm². The results were obtained as followed.

- 1) Magnitudes of cathode overpotentials varied from 630 to 1300 mV with electrolysis conditions, especially chloride ion contents.
- 2) The cathode current efficiency was over 90%, whereas the anode current efficiency varied from 50 to 90%.
- 3) The magnitude of surface residual stresses of deposits did not exceed 80MPa and the deposits obtained at 50°C showed the lowest values.
- 4) The hardness of the deposits ranged from 140 to 250 Hv whose variation could be attributed to mainly the grain sizes of the deposits.
- 5) Above about 1250mV, the deposits had randomly distributed fine grains due to the higher nucleation rate, and at 630mV had the (110) orientation with a field orientated fine structure. The deposits obtained at the intermediate overpotentials had the (100) orientation with rather coarse field oriented structures.

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