ABNORMAL GRAIN GROWTH OF ODS SUPERALLOYS ENHANCED BY BORON DOPING OR TORSIONAL STRAIN

Y.G.Nakagawa, H.Terashima, and K.Mino

Ishikawajima-Harima Heavy Industries Co., Ltd., TOKYO

Abstract

The abnormal grain growth of nickel base ODS alloys was promoted by various methods. The materials used in the study were as-extruded bars of MA6000 and Japanese experimental alloys, all of which showed no or very little grain growth by isothermal annealing. The samples were recrystallized into a large columnar grained structure using a directional zone annealing apparatus. Isothermal annealing could also induce the abnormal grain growth when:

1. a layer of nickel alloy containing boron was mounted on an end surface of a sample bar prior to the anneal, or
2. a large amount of plastic deformation was simultaneously exerted on a specimen during the anneal.

It was observed by TEM that there existed many grains with a high Cr content in the as-extruded MA6000. The recrystallized samples were free from dislocations and completely homogeneous in chemistry. The dynamical strain is considered to enhance solute diffusion for the homogenization, which is assumed to be one of the necessary conditions of triggering the abnormal grain growth.

Introduction

Oxide dispersion strengthened (ODS) superalloys are currently produced by the mechanical alloying process(1). Powders of oxides (yttria), elemental metals and alloys are mixed in a high energy ball mill to form composite powders with the dispersoid, from which bulk ODS ingots are obtained by hot extrusion. This dynamical consolidation process involving recrystallization during the extrusion is believed to give a fine grained and chemically homogeneous microstructure in the ingots. The transformation of the fine-grained structure to large elongated grains by abnormal grain growth is requisite for a superior high temperature strength of the ODS superalloys containing a large volume of γ' precipitates. The grain growth mechanism has not been well understood, but believed to be subjected to the initial (as-extruded) microstructure. The difference in the grain boundary energy is the primary driving force, but not sufficient for the coarsening in many cases where the reaction is considered to be triggered by additional factors, such as the γ' precipitate dissolution(2), oxide particle agglomeration(3), or release of the boundaries from impurity clouds (segregation). The effect of a plastic deformation

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on the grain growth has been also debated (4), but the strain energy stored by cold works in the form of high dislocation density is normally released before the transformation, and considered less important unless being induced during the heat treatment. In this paper the abnormal grain growth promoted by the zone annealing, boron doping, and high temperature deformation is described. Together with TEM microstructural studies for the as-extruded and the recrystallized ingots, some of the mechanistic discussion of the abnormal grain growth associated with the ingot production process will be introduced.

Experimental

The materials used in the present study were as-extruded bars of various nickel base ODS superalloys for which the nominal compositions are summarized in Table 1. The MA6000 is one of the commercial alloys, and an extruded sample having an 20 X 66 mm rectangular cross section was supplied by the courtesy of International Nickel Co.. The TMO-2 was developed by National Research Institute of Metals, and being used for Japanese alloy development excercises. The series of Alloy 4, 5, and 20 were also experimentally developed alloys in the authors' laboratory to study the processing parameters as a function of γ' quantity. These experimental alloys including the TMO-2 were extrusion-made at about 1050°C from attritted powders of the respective chemistries, and were supplied in the form of a 13 mm diameter bar. Some of the as-extruded samples showed no or very little abnormal grain growth by annealing at above γ' solvus temperatures, but were transformed into a large columnar grain structure by directional zone annealing. The zone annealing apparatus consisted of a 50 kHz induction heater, a pyrometer for temperature control, and a motor for travel of specimens through an induction coil. Zone anneal was done in air with typical temperature gradient of 25°C/cm across the specimen of 12 mm diameter. Iso-thermal annealing could also induce the abnormal grain growth when

1) a layer of nickel alloys containing boron was mounted on an end surface of specimen bars prior to the annealing(5), or
2) a large amount of plastic deformation was simultaneously exerted on the specimen during the annealing.

Slightly pressing amorphous tapes of Ni-15Cr-4B, or Ni-15Cr-1.7W-3.3W-1.7Ta-2.7B (wt%) against an end surface, specimens were heated in a vacuum furnace at 1200°C for 5h. The directional grain growth was observed in the materials of 5-6mm deep from the original tape interface. Small tensile bar samples with a gauge of 4 mm in diameter and 25 mm in length were machined from the as-extruded MA6000 billet, and heated at temperatures above 1100°C for 10 minutes while giving torsional deformations of various strain levels by gradually twisting the

Table 1 Chemical compositions of alloys investigated (wt%)

Alloy	C	Cr	Co	Mo	W	Ta	Al	Ti	B	Zr	Y_2O_3	Ni	γ' (vol%)
Alloy 20	0.09	14.30	-	1.75	3.66	1.77	4.15	1.82	0.025	0.09	1.1	Bal	47
Alloy 5	0.05	7.55	9.35	0.50	8.02	-	4.35	0.63	0.01	0.03	1.1	Bal	45
Alloy 4	0.05	7.20	8.25	0.51	7.79	2.14	3.24	0.60	0.01	0.03	1.0	Bal	41
TMO-2	0.05	5.9	9.7	2.0	4	2	4.2	0.8	0.01	0.05	1.1	Bal	55
MA6000	0.05	15	-	2.0	4	2	4.5	2.5	0.01	0.15	1.1	Bal	52

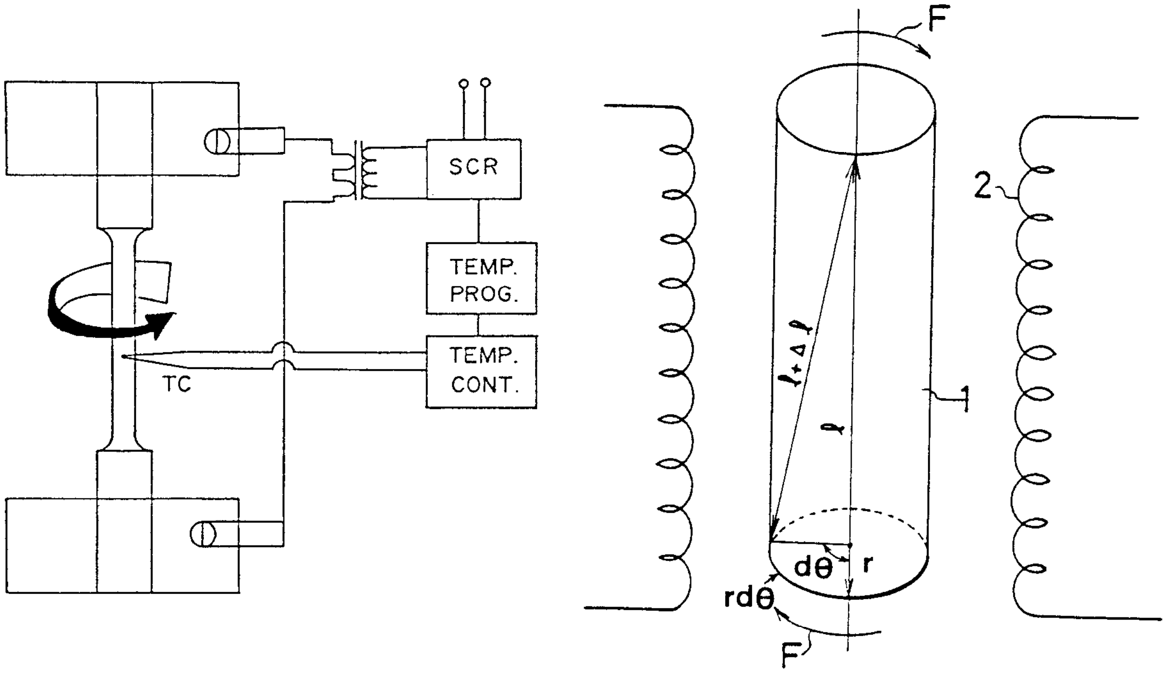


Figure 1 a) Set-up used for high temperature torsional straining
b) Definition of torsional strain (rdθ/ℓ)

samples during heating. The set-up used for high temperature straining as schematically illustrated in Figure 1(a) were built in a vacuum bell jar. Heating was done by feeding current through a sample from the grips, while a strain was exerted by mechanical rotation of the grips. The precise control of the strain level was difficult but estimated in accordance to the definition described in Figure 1(b) by which a 90 - deg. axial rotation roughly corresponded to 20% deformation on the surface. Characterization of microstructures were mainly done by transmission electron microscopy (TEM) using Hitachi 700H with EDX for micro-chemical analyses.

Results and discussion

Isothermal and zone anneal of TMO-2

The as-extruded TMO-2 samples were isothermally annealed at temperatures between 1200°C and 1290°C for 30 minutes. Extensive grain growth with some directionality parallel to the extrusion direction, were observed at temperatures above 1230±10°C. It was noted that the lower temperature anneal brought the larger grain size. For instance very large grains of up to about 15 mm in length and 4 mm in diameter were observed in the samples annealed at 1240°C, close to the possible lowest for grain growth. The similar result have been reported for MA6000. Since the final grain size is thought to be determined by the nucleation rate of new grains, less nucleation for the abnormal grain growth has occured during the anneal at the lower temperature. If abnormal grain growth is triggered by either γ' phase dissolution or oxide coarsening, it is reasonable to assume that the lower temperature anneal will give the less chance of triggering. The γ' solvus of TMO-2 determined by a differential thermal analysis, and confirmed by TEM observations, is 1150 to 1160°C. From these observations it is concluded that the γ' dissolution might be a necessary but not sufficient for the abnormal grain growth.
A cylindrical specimen of 12 mm in diameter was zone annealed at travel speed of 100 mm/h. The maximum temperature in the furnace was about 1290°C. Figure 2(a) shows the longitudinal macrostructure near the final end of the zone-annealed specimen interrupted and cooled. The grain growth interface is seen in the middle of the figure. The temperature distribution measured by thermocouples at the

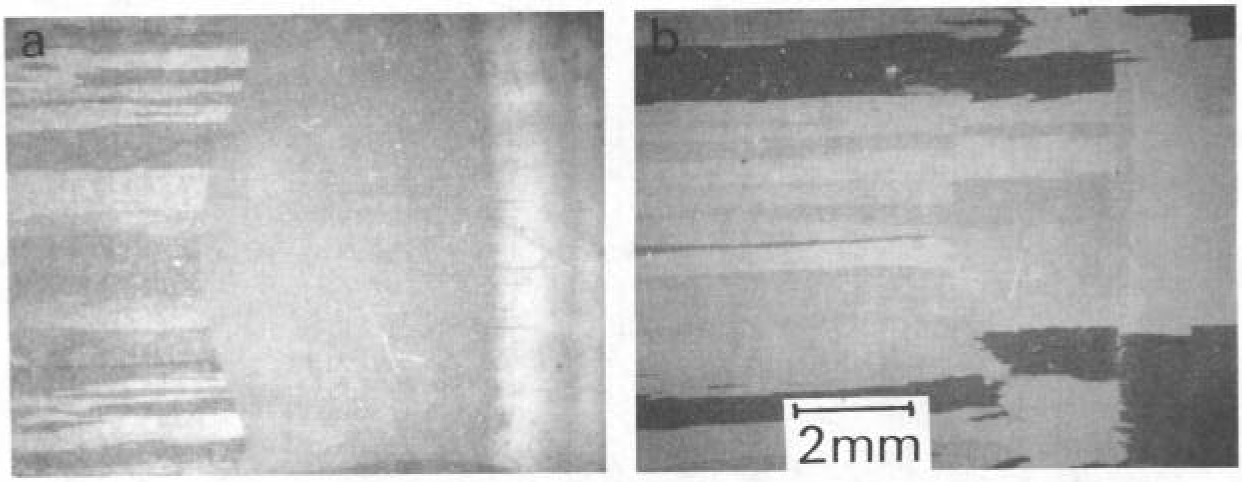


Figure 2 a) Longitudinal macrostructure of TMO-2 as zone annealed, and
b) subsequently heated isothermally at 1290°C for 10 min

surface revealed the grain growth temperature of around 1220°C. When this sample was subsequently heated isothermally at 1290°C for 10 minutes, continuous directional grain growth from the interrupted interface took place with grain discontinuity as shown in Figure 2(b). TEM micrographs were taken from a foil sliced parallel to the extrusion axis at the interface region of the zone-annealed specimen (Figure 2(a)). Figure 3 indicates the near interface structure, where the upper portion is a fine-grained area and the lower is the tip of abnormal grain growth of the columnar grains. The grain size of the fine grained region is about 0.5μm, and is not much different from the as-extruded grains. This means that the driving force for grain growth remains. Another finding was that the mean diameter of the dispersoids increased from 20 to 30 nm in the as-extruded condition to 30 to 50 nm near the interface, which would decrease back stress applied on grain growth, and thus, the dipersoid coarsening is considered as one of the secondary conditions for the grain growth triggering.

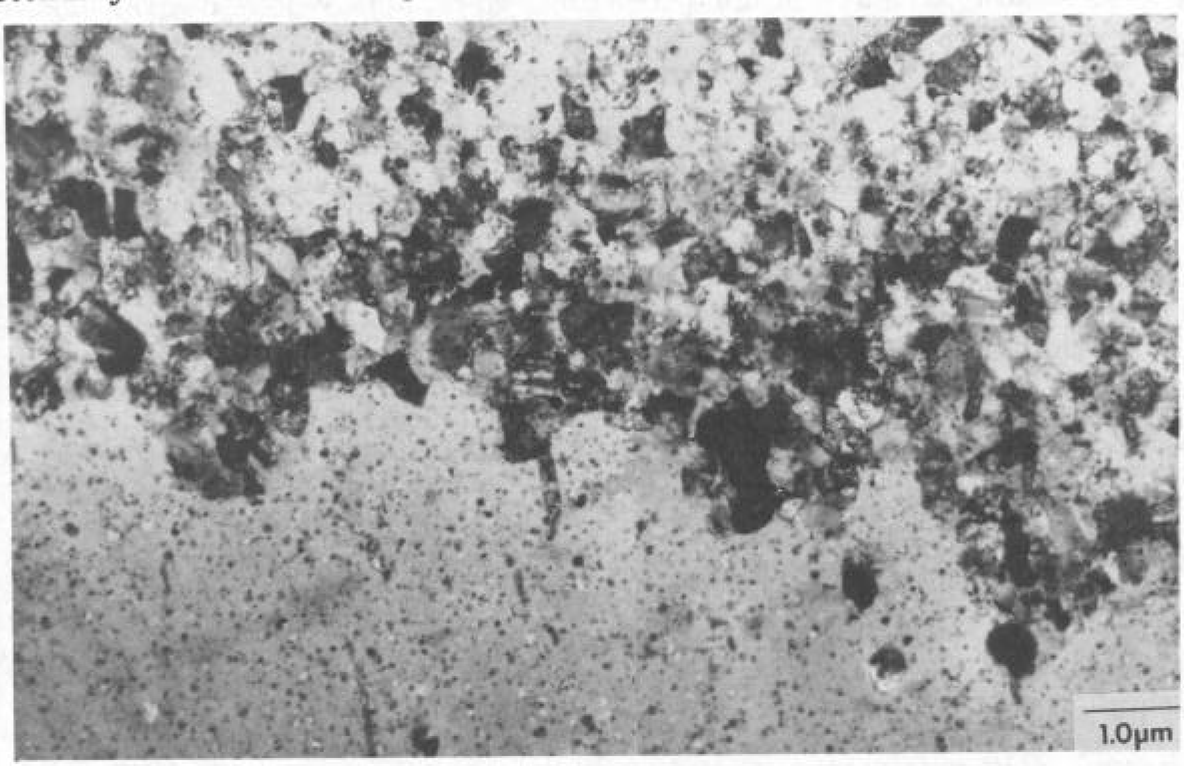


Figure 3 TEM microstructure of coarsely elongated grain and fine grain interface in the zone annealed TMO-2

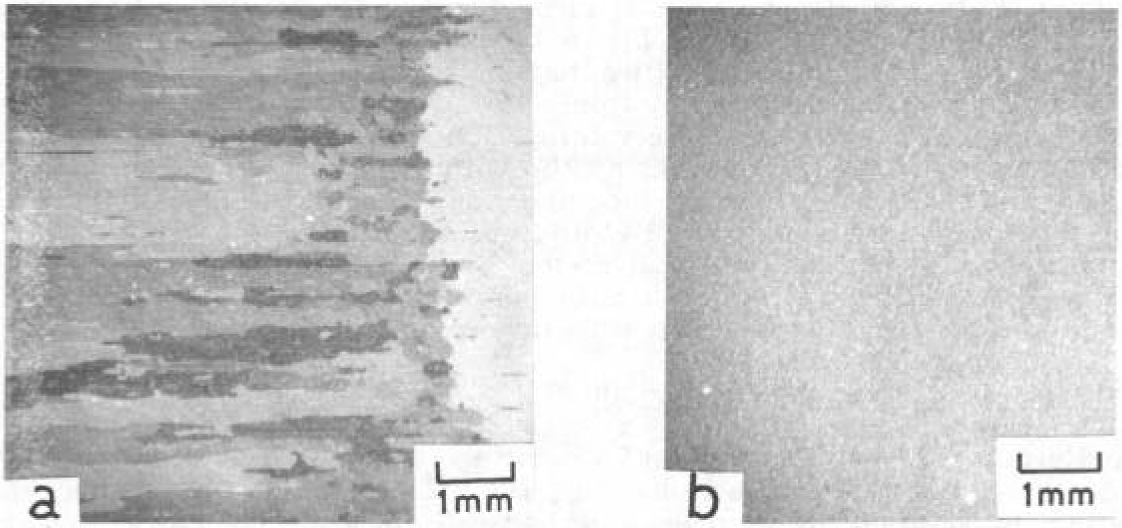


Figure 4 Longitudinal structure of Alloy 20 at 1200°C for 15h,
a) with mounting tape A, and
b) without tape

Boronizing for Alloy 4, 5, 20

The enhancement of the directional recrystallization by the boron deposition are seen in Figure 4(a) and (b), showing the longitudinal macrostructure of the Alloy 20 heated at 1200°C for 15 hours with and without boron deposition, respectively. In Figure 4(a) the tape was mounted in the left hand side of the picture, and the grain growth was developed to 6 mm in depth, which is about the distance expected for boron diffusion in nickel. No grain growth was found in the same sample without

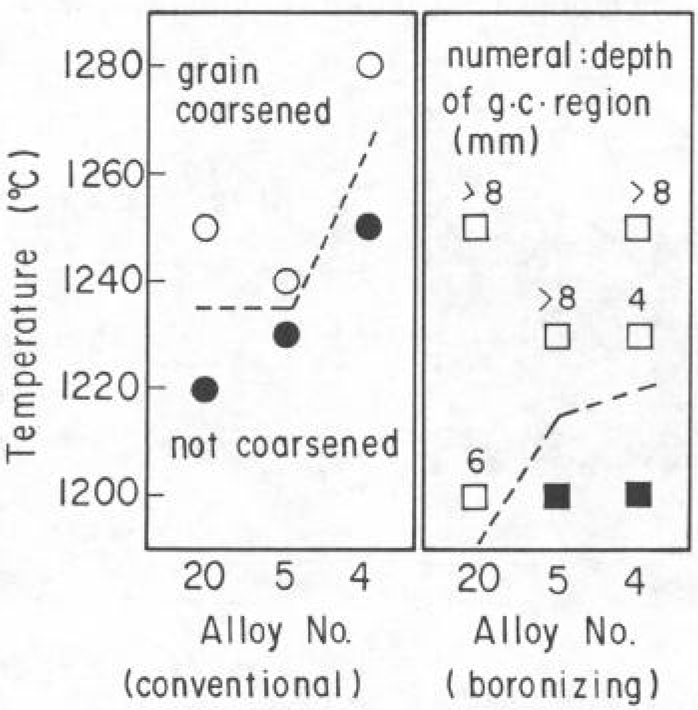


Figure 5 Effect of boronizing on abnormal grain growth temperature

boronizing (Figure 4(b)). The boron induced directional recrystallization was also found for Alloy 4 and 5. Figure 5 summarizes the results of the boronizing experiment for these alloy, suggesting that the recrystallization temperature has dropped by 20-40°C by boron doping from one end surface of the extruded bars. A possible cause of the enhanced recrystallization was initially thought due to γ' solvus temperature drop by increasing the boron content. A 300 mg slice was sampled from the boronized (near tape end) region of the Alloy 4, and from the region free from the boronizing. By differential thermal analysis for the two samples it was found that the γ' solvus for the both samples were same, and at about 1140°C. So it is concluded that the boronizing is nothing to do with the γ' solvus, and contributes to other triggering factors.

<u>High temperature straining for MA6000</u>

The material used for this experiment was the as-extruded MA6000 which could be recrystallized only by the zone annealing. Table 2 summarizes thermomechanical conditions imposed on the samples, and the resultant grain structure. When the total strain exceeded 30% and the temperature was above the γ' solvus of the alloy (1160 - 1170°C), the entire gauge length was transformed into the columnar grain structure parallel to the extrusion direction (TP13), as shown in Figure 6(a) and (b). The samples heated below the γ' solvus yielded no abnormal grain growth regardless of the strain imposition (TP08, 09), indicating importance of the γ' dissolution for the abnormal grain growth. Table 2 includes the result of microhardness measurements for the heat treated samples. Occurrence of the recrystallization was reflected in the local hardness value which dropped to near 500 Hv from 600 Hv level of the as-extruded or unrecrystallized materials. At 1180°C (above the γ' solvus), the strain level had a significant effect. When the strain was 30% or less the recrystallization took place only at a portion of the gauge length (TP12) as shown in Figure 7(a) and (b). The sample (TP10) to which 16% strain was given showed no grain growth in optical microstructures, but recrystallized grains (about 6μm) distributed in the fine grained (non-transformed) matrix were observed by TEM as illustrated in Figure 8. These recrystallized grains contained in some cases dispersoid free areas. TEM confirmed that the dislocation density in the strained but unrecrystallized specimens was low, and

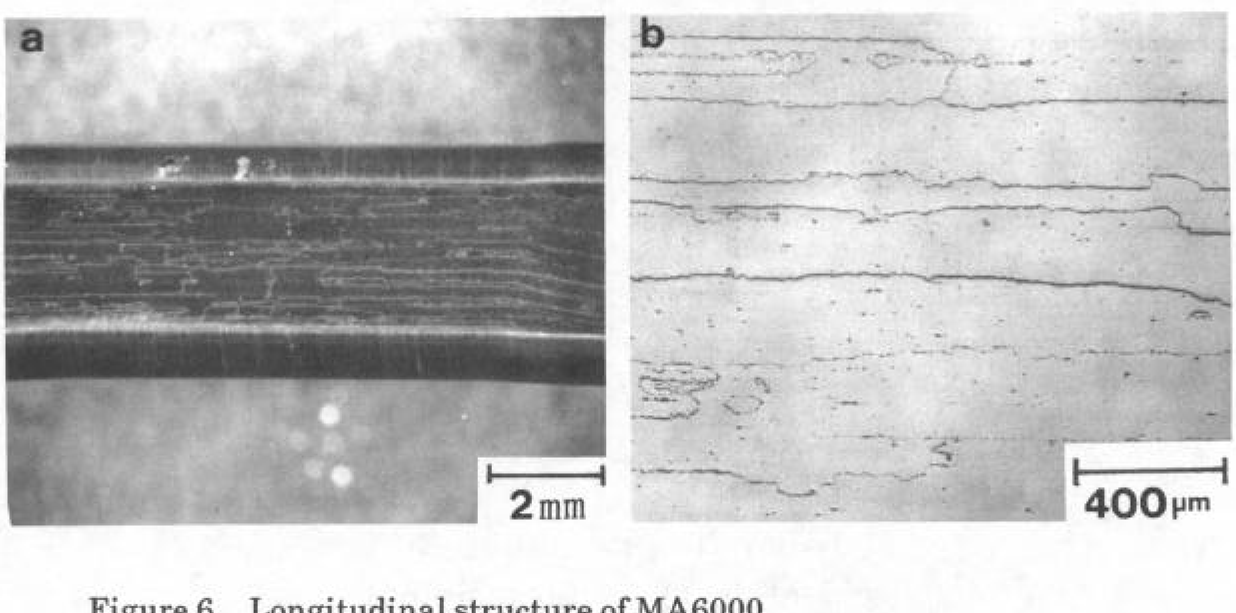


Figure 6 Longitudinal structure of MA6000
a) strain (more than 30%) anealed at 1180°C, (TP13), and
b) optical microstructure

Table 2 Thermomechanical conditions used for the high temperature straining tests and resultant macrostructure

× not recrystallized

Sample	Straining			Post-heat treatment		macro-structure	microhardness (Hv)	
	temp. (°C)	time (min.)	strain (%)	temp. (°C)	time (min.)			
08	1150	10	0			×	628	628
09	1150	5	7	1150	5	×	618	608
10	1180	5	16	1180	5	×	628	628
11	1180	10	0			×	618	628
12	1180	5	<30	1180	5	partial	505	608
13	1150	15	>30			full	513	

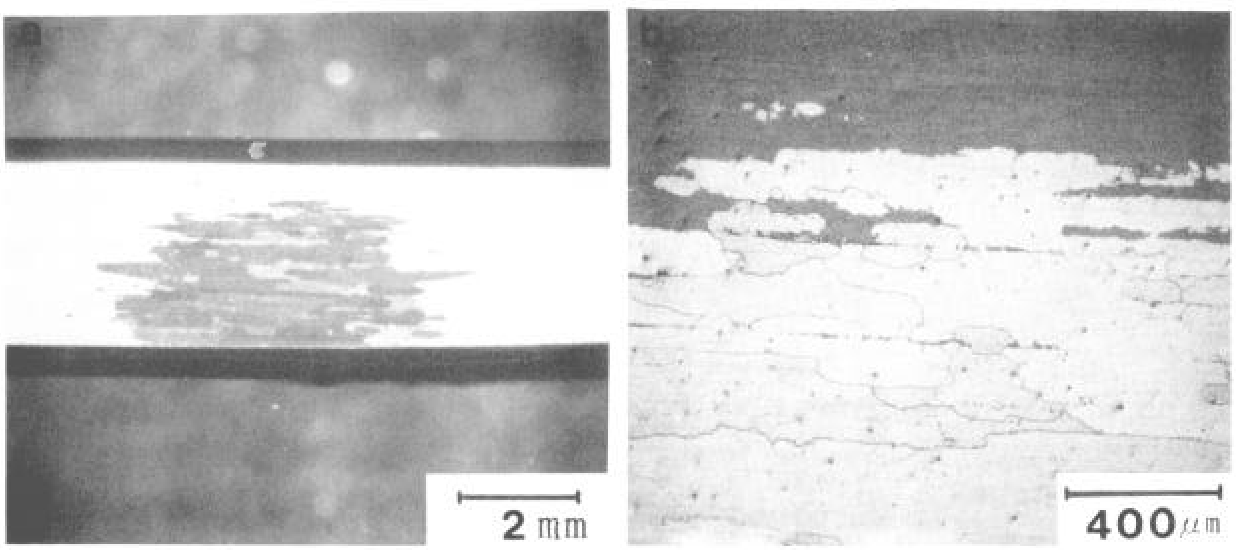
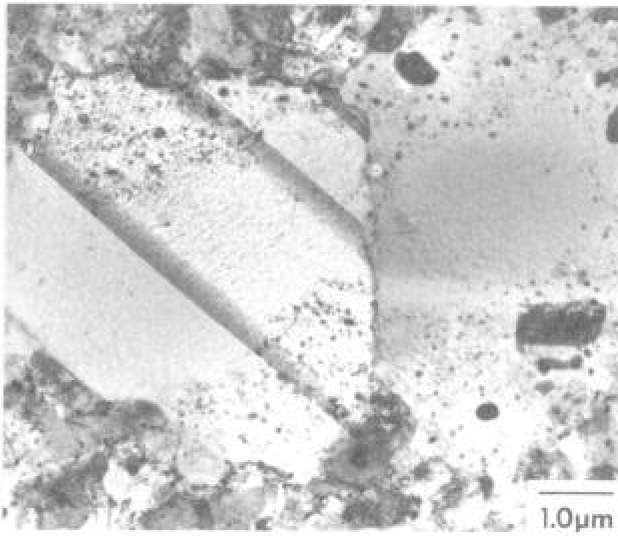


Figure 7 Longitudinal structure of MA6000
a) strain (less than 30%) annealed at 1180°C, (TP12), and
b) optical microstructure



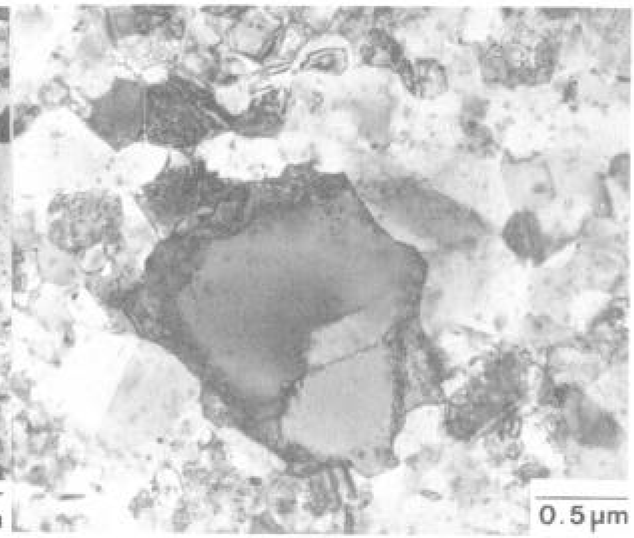


Figure 8 Recrystallized grains observed in MA6000 strain (16%) annealed at 1180°C, (TP11)

Figure 9 γ' grain observed in the as-extruded MA6000

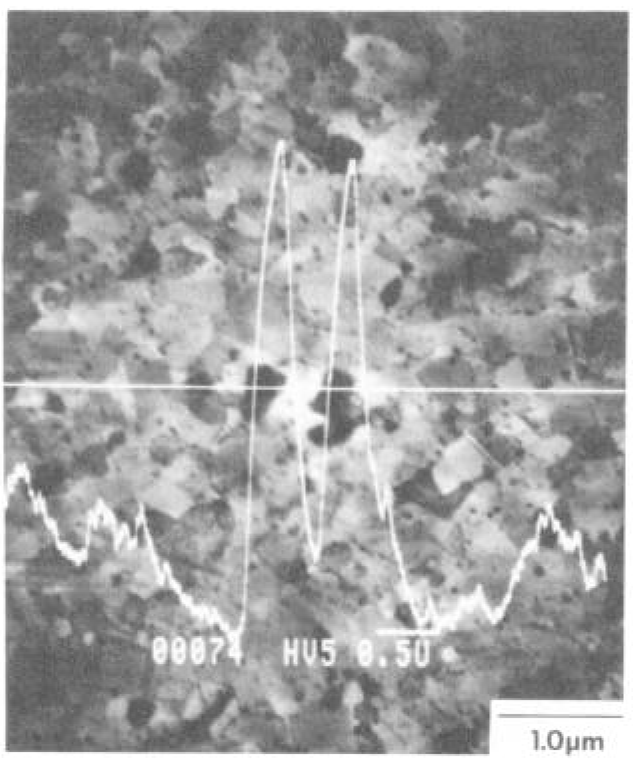


Figure 10 High Cr content grains in the as-extruded MA6000 (Cr line)

about equivalent to that of the fine grained structure of the as-extruded material. It was also observed by EDX and selected area diffraction that there existed many γ' grains (Figure 9) and grains with high Cr contents (Figure 10) in the as-extruded material. This implies that there is a strong chemical inhomogeneity in the microstructure. The γ' grains is a common feature of PM parts of high γ' nickel alloys. A typical composition of the high Cr grains measured by EDX was 75Cr-5Mo-15Ni (wt%). However, in the non-transformed area of the partially recrystallized samples (TP10, 12), non of the high Cr grains were found. The recrystallized samples were found about free from the dislocations and completely homogeneous in chemistry. Thus it is reasonable to assume that the abnormal grain growth must be preceded by the dissolution of the high Cr grains, which can be done by solute diffusion process. The roll of the strain is considered to enhance the diffusion by a number of means. The simplest model would be the pipe diffusion along the introduced dislocations, or excessive vacancies created by dislocation reactions. However the dislocation density observed in the strained sample was not much different from that in the unstrained, and not more than the density ($>10^{10}/cm^3$) normally required to see the effect. This suggests that the deformation was likely associated with the grain boundary, namely superplastic flows driven by boundary sliding and rotation where the solute transport through boundary diffusion is highly active. The recrystallization enhanced by boron doping may also related with the homogenization of microchemistry, since the amorphous tape was initially melted at the start of the heat treatment, which would reduce the chemistry difference at the near tape region.

Conclusions

1. The γ' dissolution is a necessary condition for the abnormal grain growth of nickel base ODS alloys containing a large amount of γ'.
2. It seems that the oxide coarsening triggers the grain growth.
3. The boron doping enhanced the directional recrystallization by isothermal annealing.
4. High temperature straining above the γ' solvus enhanced the directional grain growth.
5. In the as-extruded materials and the materials which did not show the grain growth, there were many grains with high Cr content. Non of them were found in the unrecrystallized region of the partially recrystallized materials.
6. The effect of the high temperature strain is considered to promote the chemical homogeneity prior to the recrystallization, which seems another triggering condition for the abnormal grain growth.

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