Dispersion Strengthened FeCrAlY Alloys By Flake Powder Processing

by

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ABSTRACT

   A novel, high yield, powder metallurgy technique
involving high energy (attritor) milling was utilized to
produce oxide dispersion strengthened FeCrAlY alloys
without the concurrent formation of chromia or chromia-
containing spinels. The technique utilizes attritor
milling of atomized powder/organic surfactant slurries, in
air, to produce flake-like shaped particles with large
specific surface areas. It is the oxidation of these
powder surfaces under ambient conditions that ultimately
generates the dispersoid.

   Consolidation of powder compacts was accomplished
by hot extrusion at either 982°C or 1093°C. The dispersoid
present in as-extruded bar was identified as $3Y_2O_3 \cdot 5Al_2O_3$
(yttrium-aluminum garnet) with an average particle size
of about 300Å. As-extruded 982°C tensile and stress
rupture properties were significantly improved when
compared to the same composition without dispersoid.

   Further improvement in stress-rupture strength was
obtained by producing coarse grain structures with high
aspect ratio. Two of the alloys produced responded to
secondary grain growth in the as-extruded condition by
both isothermal annealing and directional recrystallization.

INTRODUCTION

The increasing demand for high temperature materials with superior strength and surface stability has focused attention on oxide dispersion strengthened (O.D.S.) superalloys. The vast majority of O.D.S. alloys are produced by powder metallurgy techniques. Since conventional superalloys contain elements Ti, Al and Cr that readily form oxides which are difficult to reduce once formed, the possibility exists for excessive oxygen contamination by uncontrolled oxidation of the powder charge during processing. Prior investigations[1,2,3] have utilized selective reduction as a means of controlling the oxygen content of selected O.D.S. alloys. However, in the case of superalloy compositions, reduction of unwanted oxides is not possible and therefore must be avoided. "Mechanical alloying"[4] represents the first successful means of incorporating a uniform oxide dispersion into superalloy-type compositions by powder metallurgical techniques. Allen[5] has demonstrated that controlled surface oxidation of prealloyed, inert gas atomized FeCrAlY powders is capable of producing O.D.S. alloys with a respectable combination of high temperature strength and oxidation resistance. Another technique, flake powder processing by attritor milling has been successfully applied to O.D.S. copper[6] and nickel[7] alloys which contained only one strong oxide forming element. The technique involves a surface oxidation effect similar to the SAP (sintered aluminum powder) method. However, instead of utilizing the oxide formed from the base metal as a dispersoid (Al_2O_3 for SAP) the starting powder composition is preselected to yield, after processing, a stable oxide dispersoid.

Higher dispersoid content and improved distribution, compared to surface oxidation of as-atomized spherical powders, are possible if the powder particles possess a high surface area to volume ratio and a minimum dimension which is of the order of the desired interparticle spacing (0.1-0.01μm for O.D.S. alloys). These requirements are met by a flake-shaped particle which is easily produced by wet ball milling or attritor milling.

In the case of superalloys, the question of which surface oxides will form as a result of the milling process is difficult to answer. Clearly, the most desirable result would be to generate only the most stable oxides since the need for reduction of other oxides is thus eliminated. The iron-chromium-aluminum-yttrium (FeCrAlY) system was selected for this investigation with the expectation that its ability to form strongly adherent alumina scale would be of advantage from a processing standpoint. The objectives of the program were to generate an alumina dispersion in FeCrAl matrix by wet attritor milling without concurrently producing Fe or Cr oxides and then to assess the effect of the dispersion on high temperature properties; no attempt was made to optimize final alloy properties.

EXPERIMENTAL PROCEDURE

Argon atomized Fe-25Cr-4Al-1Y prealloyed powder of -60 mesh (-250μm size was obtained for this investigation (see Table I). A 450g trial batch of

Table I
Summary of Compositional Data

Alloy	Particle Size Microns	W/% Cr	W/% Al	W/% Y	W/% O	W/% C	V/% Dispersoid[1]
As-Rec'd	-250	25.0	4.1	1.5	0.03	-	--
A	-250	25.1	4.2	1.3	0.02	0.03	--
B	-150, +63	24.7	3.8	0.8	0.98	0.04	5.0
C	-150, +63	24.3	4.0	1.0	0.55	0.04	2.9
D	-63	24.2	1.4	0.4	2.25	0.10	10.6

(1) Assumed to be 100% $3Y_2O_3$ $5Al_2O_3$ YAG (Yttrium-Aluminum-Garnet).

powder was attritor (Segvari Type 1-S) milled for 72 hours. At approximately
3-4 hour intervals, the attritor was stopped, the powder separated from the
grinding balls, the attritor restarted and the powder added. This was done
to insure that the entire powder charge was subjected to the attritor
milling action. After milling, the powder charge was sized, hot outgassed
in vacuum, and vacuum fusion oxygen analysis as well as specific surface
area measurements (continuous flow method[8]) made. Based on this data,
powder for the actual alloys was prepared from approximately 450g charges
of -60 mesh powder ground for 6-8 hours and sieved for size. Oversized
flakes were recharged while these which were undersized were utilized for an
alloy prepared from the milling fines.

The milled powders were loaded into mild steel extrusion containers and
cold pressed to 60-70% density. After pressing, a top cover with evacuation
tube was welded into place and the entire assembly leak tested with a mass
spectrometer leak detector. The billets were vacuum outgassed at 538°C and
sealed from the vacuum system under a dynamic vacuum of about 5μm Hg. A
schematic flow diagram for the powder processing is given in Figure 1. Prior
to extrusion, all billets were soaked at 1093°C/2 hours. Table II details
the processing conditions along with pertinent extrusion data. All extrusions
were checked for soundness by x-ray.

Standard metallographic techniques were used to evaluate the microstructure
of extruded and extruded + heat treated specimens. A 10% oxalic acid solution
was more effective for etching fine grain material while Kalling's etchant
proved to be the most effective for determining coarser grain structures.
The dispersoid crystal structure and composition were determined by x-ray
diffraction (CoKα). Particle size, distribution and morphology were
qualitatively determined by transmission electron microscopy. The vacuum
fusion technique was used for oxygen analysis of as-extruded alloys.
Selected specimens were examined directly by transmission electron microscopy.
Thin foils were prepared by twin jet electrothinning using a 10% perchloric
acid - 90% glacial acetic acid electrolyte.

Isothermal annealing and directional recrystallization were utilized for
grain coarsening studies. Mechanical testing consisted of 982°C tensile
testing of as-extruded alloys as well as 982°C and 1093°C stress-rupture
testing of all alloys with various post extrusion treatments.

RESULTS AND DISCUSSION

Processing

Attritor milling has a marked effect on the spherical as-atomized powder.
Figure 2 demonstrates that the powder shape has been altered to flake by the
action of the attritor mill. Concurrent with this shape change, the oxygen
content of the milled powder was observed to increase with decreasing particle
size (see Figure 3). Oxygen content was also observed to increase with
increasing specific surface area (Figure 4). Thus, the change in oxygen
content is clearly related to a surface oxidation effect and not to bulk or

Table II
Extrusion Data

Alloy	Extrusion Temp. °C	Ratio	Ram Speed in/min.
A	984	17.8	160
B	984	17.8	160
C	1093	17.8	205
D	990	17.8	160

complete oxidation of the powder charge. The data presented in Figures 3
and 4 allow the "calibration" of the alloy system and permit selection of
dispersoid volume fraction by control of oxygen content. The milled powders,
including the -230 mesh (-63μm) fines, were not pyrophoric and exhibited no
additional oxygen pick-up (despite air storage) in the interim (∿2 weeks)
between milling and pressing into billets. The milling action produced
particle thicknesses which were transparent to a 100 KV electron beam, thus
this dimension was of the order of 0.1-0.3μm.[9] An Al_2O_3 volume fraction of
0.03-0.04 was selected for this study and corresponds to about 0.65-0.85 w/o
oxygen in the processed powder. Reference to Figure 3 indicates that this
oxygen level corresponds to a -150 μm to +63μm size fraction. Powder from
this size fraction was used to produce alloys B and C (see below).

   The attritor milling technique utilized for this study yielded approximately
75% useful powder in the size range of primary interest (alloys B and C).
Based on the data, it appears to be a straightforward step to modify the
milling process to a continuous one by introduction of a recirculation system
and milling the powder charge for preselected times to achieve the desired
oxygen levels. Yields from this type of processing could logically be
expected to be greater than 95%.

   An important result of this study is the realization that a prealloyed
powder such as FeCrAlY (2541) can be attritor processed as a slurry in air
without the occurrence of significant Cr_2O_3 contamination. Samples of milled
powders were tested for the presence of oxide(s) after various treatments
which are described in Table III. The oxide was obtained by dissolving the
treated powders in hot dilute HCl and centrifuging the residue. This residue
was then identified by x-ray diffraction. As Table III indicates, no oxides
were detected on as-attrited powder, however αAl_2O_3 and yttrium-aluminum-
garnet (YAG) were detected after a 1093°C/3 hour treatment in a vycor
encapsulation backfilled with 1/3 atmosphere of argon. The data tend to
indicate the nature of the surface oxidation reaction. It is quite
conceivable that the reaction takes place in two or more steps; first an
adherent, amorphous alumina gel forms during milling and then transforms
upon heating to crystalline alumina[10], further heating then results in
the formation of YAG.

   The alloys produced in this study are identified in Table I. Alloy A was
produced from as-atomized, unmilled powder and was used as a "reference" alloy.
Alloys B and C, nominally 4 v/o Al_2O_3, were made from a split batch of attrited
powder. The only processing variable which differentiates these alloys is
extrusion temperature (982°C versus 1093°C). Alloy D was produced from the
-63μm milling fines. X-ray inspection confirmed the overall soundness of
the extruded bars.

   ### As-Extruded State

   Metallographic inspection of the four as-extruded alloys revealed
differences between them. For example, alloy A (as-atomized powder)
possessed a fine (about 10μm) relatively equiaxed grain structure. The alloy

Table III
Extracted Phases Present After Various
Stages of Processing

Condition	Observed Phases
Attrited + Vacuum Dry	None
Attrited + 550°C/2 hrs/Ar + 1093°C/3 hrs/Ar	αAl_2O_3 + trace $3Y_2O_3 \cdot 5Al_2O_3$ & $Cr_{23}C_6$
As-Extruded (Alloys B, C and D)	$3Y_2O_3 \cdot 5Al_2O_3$ + trace αAl_2O_3 & $Cr_{23}C_6$

contained an even distribution of the iron-yttrium intermetallics (Y_2Fe_{17} and YFe_5).[11] Alignment of the intermetallics parallel to the extrusion direction was apparent in the longitudinal section. Unprocessed prior atomized powder particles could be discerned by the needle-like distribution of the intermetallic particles.

Alloys B and C differed considerably from alloys A and D, but were similar to each other structurally. The Fe-Y intermetallics were present with what appeared to be a similar distribution to that of alloy A. Individual oxide particles cannot be resolved; however, the fine striated appearance characteristic of an oxide dispersion was evident. Although difficult to verify, it seems that the grain size of alloy B (extruded at 982°C was somewhat finer than that of alloy C at 1093°C). The as-extruded grain sizes of both alloys (B&C) were about 5-10 microns. Both alloys B and C possessed an occasional "needle-like" area similar to alloy A. These areas are indicative of the incorporation of an unprocessed powder particle.

Alloy D (produced from minus 63μm "fines") displayed the most refined as-extruded structure of the four alloys produced. A considerable size reduction of the Fe-Y intermetallic phases was apparent as well as the absence of the needle-like areas present in the other three alloys. A fine background of oxide particles was also evident.

In all alloys except alloy "A" the dispersoid was identified as $3Y_2O_3 \cdot 5Al_2O_3$ + trace Al_2O_3. A small amount of $Cr_{23}C_6$ was also present (see Table I). Considerable line broadening was observed in the x-ray diffraction patterns which indicates a fine $< 500\text{Å}$ particle size.[12] The change in major oxide phase from αAl_2O_3 to YAG after extrusion may be due to an additional reaction during extrusion or to a solid-state reaction similar to that observed by Benjamin et al.[13]

Tension testing was done on an Instron tensile testing machine at a constant cross head speed of 0.02 cm/min. except for alloy A which was tested at 0.002 cm/min.. The data are summarized in Table IV. Results of stress-rupture testing of as-extruded alloys are presented in Figures 5 and 6. Alloy B (5 v/o YAG) displayed an eighteen-fold increase in stress for 100 hour rupture life compared to unmilled alloy A. Alloy C (2.9 v/o YAG) was about 11 times stronger than alloy A on the same basis. The difference in stress rupture strength between alloys B and C appears to be related to differences in volume fraction dispersoid after extrusion and extrusion temperature (see Table I).

Grain Coarsening Behavior and Properties

Isothermal Annealing

Secondary recrystallization[14] (or exaggerated grain growth) in O.D.S. materials leads to anisotropic grain size with high aspect ratio (ℓ/d). In most cases the ratio of longitudinal diameter (ℓ) to transverse diameter (d) should generally be greater than 3 to produce substantial improvement in high

Table IV
982°C Tensile Data For As-Extruded Alloys

Alloy	Vol. % Oxide	UTS (MPa)	0.2 Y.S. (MPa)	% El.	% R.A.
A	–	17.1	3.9	166.0	95.5
B	5.0	42.7	36.5	36.4	94.7
C	2.9	46.2	40.0	41.2	94.7
D	10.6	62.7	60.0	13.0	10.0

temperature properties.[15] Under ideal conditions the grain aspect ratio may exceed ten. Annealing in air at 1316°C, near the incipient melting point (∿1360°C) of FeCrAlY (2541), was used to determine secondary recrystallization response. Figure 7 shows photomicrographs of longitudinal sections of alloys B and C after annealing at 1316°C for 1.5 hours.

The key structural change for alloy B was an increase in longitudinal and transverse grain sizes. The longitudinal dimension although difficult to determine accurately, was in the 150-200μm range while the transverse grain diameter is about 40μm (ℓ/d ∿4.5). The fine, background oxide dispersoid was evident, but appeared to be absent in localized regions throughout the bar. A few clusters of much smaller grains are also present throughout the specimen volume. Although frequently associated with regions apparently lacking dispersoid, these fine grain areas were also observed in regions where dispersoid was present.

Alloy C (Figure 7) responded to the isothermal anneal in a manner similar to alloy B. An elongated grain structure was also present after annealing. The transverse grain diameter was about 35 microns while the longitudinal grain dimension was about 200 microns (ℓ/d ∿5). Fine, relatively equiaxed grains were observed to be completely surrounded by much larger grains. As in alloy B, the iron-yttrium intermetallic particles have coarsened and generally appear to be located at grain boundaries. Regions apparently lacking dispersoid were also observed for alloy C. Alloys A and D which contained 0 and 14% dispersoid respectively, did not show a significant change in grain size or shape as a result of the isothermal anneal.

Alloys B and C which had been isothermally annealed in air at 1316°C/2 hours were stress rupture tested at 982°C. The results were plotted in Figures 5 and 6.

If one compares isothermally annealed to as-extruded material it is apparent that a substantial improvement in high temperature stress rupture strength has been achieved as a result of the isothermal annealing treatment and the associated microstructural features which were developed. For example, alloy C as-extruded which had a stress for 100 hour life at 982°C of 15.2 MPa has been increased to 40.7 MPa.

The fact that alloys B and C display grain growth as a result of isothermal annealing is of particular interest and advantage. Allen[5] had considerable success with O.D. FeCrAlY alloys which had been grain coarsened by extensive thermo-mechanical processing followed by directional recrystallization. His investigation did not produce an O.D. alloy which would grain coarsen as a result of isothermal annealing. The only other alloy systems produced to date which respond similarly are of the "mechanical alloy" genera.

Directional Recrystallization

Directional recrystallization is another method for the solid state generation of oriented microstructures and has proven to be effective in furthering the high temperature strength of O.D. alloys.[16] The technique is especially useful for generating a grain structure with high aspect ratio (ℓ/d) in O.D. alloys which have been previously processed in such a way that they will not respond (exaggerated grain growth) to isothermal annealing. The directional recrystallization apparatus used in this investigation is similar to that used by Allen.[16]

Extruded bar specimens approximately 0.95 cm ϕ by 20 cm long were directionally recrystallized at rates of 5cm hr^{-1} and 18-20cm hr^{-1}. The maximum temperature in the hot zone was 1343°C for all runs. Figure 8 shows macro-etched specimens of alloys B and C which had been directionally recrystallized at 18cm hr^{-1}. As can be seen, significant grain growth has

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occurred. The overall grain structure is one of a bundle of thin, pencil-
like grains of varying lengths, many growing the entire length of the bar.
The grain aspect ratio is estimated to be in the range of 15-30 for both
alloys and both recrystallization rates. The longitudinal structures of
the isothermally annealed material, contained fine, equiaxed regions which
were found to be relatively free of dispersoid. In most cases, these fine
grain regions were surrounded or engulfed by a single, much larger grain.
The iron-yttrium inter-metallic phases have coarsened and are associated
mostly with grain boundary regions. Due to the difficulty of finding a
suitable grain boundary etchant, it was nearly impossible to identify and
follow individual grains in a metallographic section.

Dispersoid distribution was qualitatively determined by transmission
electron microscopy in alloys B and C which had been directionally
recrystallized at $1343°C/18cm$ hr^{-1}. Figure 9 shows a typical transverse
structure for both alloys. In general, the distribution of the dispersoid
was excellent. No evidence of agglomerated oxides was observed. The
observed "in situ" particle size was found to range from about 100Å - 2000Å
with the majority of the particles in the $200-300\text{Å}$ size range. A larger
($\sim1\mu m$) blocky phase was also observed in the thin foils and was randomly
distributed throughout the matrix. This phase is thought to be Y-Fe
intermetallics. A unique feature of the dispersoid distribution was the
occurrence of "stringers" or lines of dispersoid (as near circled area in
Figure 9). In many cases, the lines were observed as nearly parallel pairs
with a spacing of about $0.1-0.3\mu m$. The overall matrix dislocation
structure appeared to be typical of a recrystallized ferritic alloy.
Localized fine grained regions were also observed in the foils.

Alloys B and C processed by directional recrystallization displayed a
further increase in stress-rupture strength (Figures 5 and 6). In fact,
the strongest material produced in this study had been directionally
recrystallized. Directional recrystallization resulted in grain structures
with very high aspect ratios ($\ell/d \sim 30$). Furthermore, the occurrence of
fine equiaxed grain regions which were observed in the isothermally
annealed alloys was substantially decreased. The improvement in stress-
rupture strength as a result of directional recrystallization is most
probably due to the grain size increase and elimination of a major fraction
of the fine, equiaxed grains. Although a substantial improvement in stress-
rupture properties compared to as-extruded material was observed, the
improvement was only about 15 percent greater than that obtained by
isothermal annealing. Similar results have been obtained for mechanically
alloyed nickel base alloys. [17]

SUMMARY AND CONCLUSIONS

It has been demonstrated that a powder metallurgy technique involving
attritor milling can be utilized to generate an inert oxide in an alloy
matrix containing significant amounts of chromium and aluminum without the
formation of chromia or chromia-containing spinels. Oxide formation
apparently occurs on the surface of each individual powder particle and
is only surface related. The milling procedures employed resulted in a
small fraction of unmilled material included in the consolidated bar and
ultimately to fine grain regions after recrystallization.

Two of the alloys produced in this investigation represent the only
other O.D. materials which respond to isothermal and gradient annealing
by secondary recrystallization in the as-extruded condition. Only materials
processed by mechanical alloying respond in a similar manner.

The alloy structures are characterized by a fine (less than 500Å) uniform
dispersoid of discrete $3Y_2O_3 \cdot 5Al_2O_3$ (yttrium-aluminum garnet). Iron-yttrium
intermetallic phases as well as small amounts of $Cr_{23}C_6$ were present in the

alloys studied. The YAG dispersoid possesses excellent high temperature stability (i.e. resistance to particle coarsening) and is clearly suitable as a dispersoid.

Specifically, the following conclusions can be made as a result of this study:

1. Flake powder processing is capable of generating uniform, inert oxide dispersions in FeCrAlY (2541) without chromia contamination.

2. Oxide formation takes place as a result of surface reaction(s).

3. FeCrAlY alloys produced by this technique are capable of secondary and directional recrystallization in the as-extruded condition.

4. The dispersoid present in the consolidated alloys is $3Y_2O_3 \cdot 5Al_2O_3$ (yttrium-aluminum garnet).

5. Alloys with improved stress-rupture strength have been produced utilizing this technique.

6. Large grain size and high aspect ratio have a major beneficial effect on the high temperature strength of O.D. FeCrAlY alloys.

ACKNOWLEDGEMENTS

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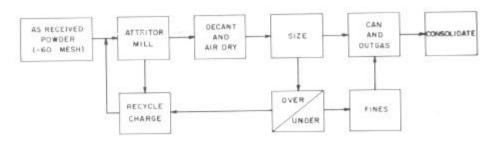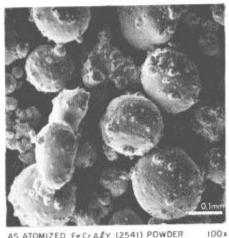17. R.L. Cairns, et al: Met. Trans., 1975, vol. 6A, p. 179.

FIGURE I. SCHEMATIC FLOW DIAGRAM FOR POWDER PROCESSING

AS ATOMIZED FeCrAℓY (2541) POWDER 100x

ATTRITED FeCrAℓY 6-8 HRS 50x
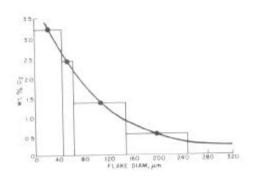
FIGURE 2. EFFECT OF ATTRITOR PROCESSING ON PARTICLE SHAPE

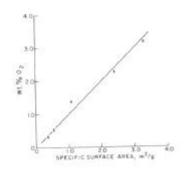FIGURE 3 OXYGEN CONTENT VERSUS PARTICLE SIZE FOR ATTRITED POWDERS

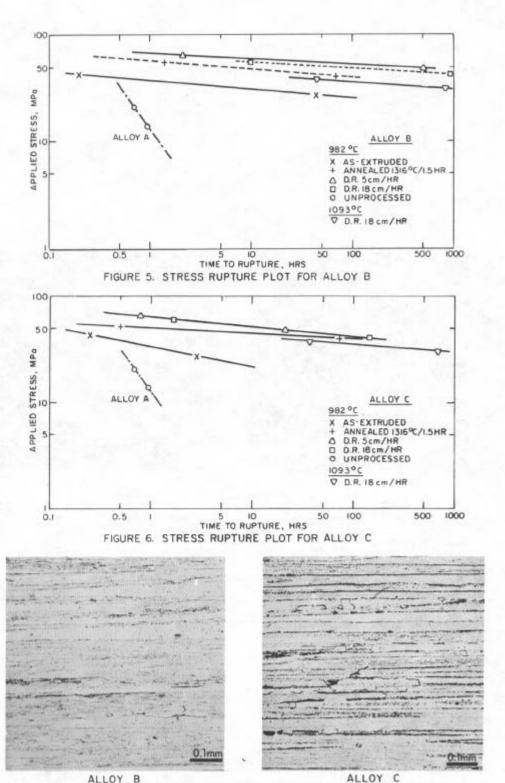FIGURE 4 OXYGEN CONTENT VERSUS SPECIFIC SURFACE AREA FOR ATTRITED POWDERS

FIGURE 5. STRESS RUPTURE PLOT FOR ALLOY B

FIGURE 6. STRESS RUPTURE PLOT FOR ALLOY C

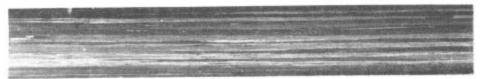ALLOY B   ALLOY C

FIGURE 7. STRUCTURE AFTER ISOTHERMAL ANNEALING AT 2400°F/1.5 HRS
(LONG SECTION) ETCHANT: 10% OXALIC   100 x

BAR NO. B

BAR NO. C

FIGURE 8. ALLOYS B AND C DIRECTIONALLY RECRYSTALLIZED AT 2450°F/7"HR⁻¹
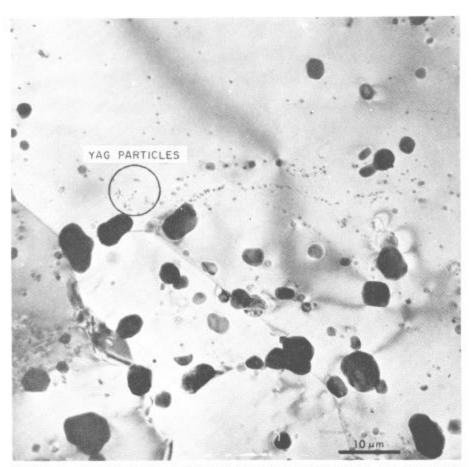~3x   ETCHANT: STRONG FeCℓ₃

YAG PARTICLES

10 μm

FIGURE 9. TRANSMISSION ELECTRONMICROGRAPH OF ALLOY B DIRECTIONALLY
RECRYSTALLIZED AT 1343°C/18 cm HR⁻¹ (TRANSVERSE SECTION)
50,000 x