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# A STUDY OF THE OXIDE DISPERSION AND RECRYSTALLIZATION IN NiCrAl PREPARED FROM PREOXIDIZED POWDER

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ABSTRACT

The SAP technique of dispersion strengthening (formation of an oxide dispersion by preoxidation of metal powders) was applied to atomized powder of the alloy Ni-17Cr-5Al-0.2 Y. SAP-NiCrAl was worked by extrusion and rod rolling at $1205^\circ$ C and by swaging at $760^\circ$ C. A variety of annealing treatments were applied after working to determine the recrystallization response. NiCrAlY, similarly prepared from atomized powder, but without a preoxidation treatment, was examined for comparison. The SAP-NiCrAl of this study exhibited oxide particle size and spacing much larger than that usually observed in oxide dispersion strengthened alloys; nonetheless, it was possible to achieve abnormal (secondary) recrystallization in the SAP-NiCrAl as has been reported for other oxide dispersion strengthened alloys. In contrast, unoxidized NiCrAlY exhibited only primary recrystallization.

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# A STUDY OF THE OXIDE DISPERSION AND RECRYSTALLIZATION

## IN NiCrAl PREPARED FROM PREOXIDIZED POWDER

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## SUMMARY

This study[*] was undertaken to investigate both the nature of the
oxide dispersion in NiCrAl prepared from preoxidized powder and the re-
crystallization processes occurring in oxide dispersion strengthened
NiCrAl so prepared. In this process, referred to as the SAP technique,
an oxide dispersion is formed by partial oxidation of metal powders be-
fore consolidation. In this study, prealloyed powder of the Ni-17Cr-
5Al-0.2 Y composition was partially oxidized to form one volume percent
of oxide dispersoid. The powder was consolidated by extrusion and fur-
ther worked by rod rolling followed by swaging. For comparison, the
same processing steps were applied to unoxidized NiCrAlY powder.

The oxidized powders were examined by scanning electron and trans-
mission electron microscopy. The consolidated SAP-NiCrAl was evaluated
by electron microscopy. The response of both unoxidized NiCrAlY and
SAP-NiCrAl to annealing treatment was determined as a function of time
and temperature with concentrated attention being given to swaged SAP-
NiCrAl.

The oxide particles derived by use of the SAP technique were coarser
and more widely spaced than desired for good dispersion strengthening.

Nonetheless, the process of abnormal (secondary) recrystallization was shown to occur in the swaged SAP-NiCrAl. In contrast the recrystallization response of unoxidized NiCrAlY was consistently normal (primary) recrystallization. Although the oxide size and spacing in SAP-NiCrAl were an order of magnitude greater than in TD-Ni or TD-NiCr the same relation between primary recrystallization grain size, dispersoid parameters, and occurrence of abnormal recrystallization was observed.

It is suggested that a process using a small volume fraction of coarse dispersoid might be beneficially applied to encourage recrystallization to large grains in otherwise difficult to recrystallize powder metallurgy superalloys.

## INTRODUCTION

Elevated temperature creep res_stance in oxide dispersion strengthened (O.D.S.) materials appears to depend on at least two factors: a fine dispersion of stable oxide particles and a special microstructure of large interlocking grains, well elongated in the direction of the major use stress. Fine dispersions have been achieved by many means including oxidation (refs. 2, 3, and 4), chemical (refs. 5 and 6), and mechanical (refs. 7 and 8) methods. The formation of large grains has been shown to occur in TD-Ni (ref. 9) and in TD-NiCr (ref. 10) by the process of abnormal recrystallization. In this process a few grains grow at the expense of all the rest (Ref. 11). The process is termed secondary recrystallization, abnormal recrystallization, or exaggerated grain growth.

The objective of this study was twofold:

(1) To determine the nature of the oxide dispersion achieved by preoxidizing NiCrAlY powder (to form oxide dispersion strengthened NiCrAl) and

(2) To determine if secondary recrystallization occurs in a consolidated material made from such preoxidized powder.

Comparisons were made to oxide-free NiCrAlY also processed by the same powder metallurgical techniques.

A nickel alloy containing 17 weight percent chromium and 5 weight percent aluminum was chosen for this study because the excellent oxidation resistance of such alloys (ref. 12) makes them candidate materials for advanced gas turbine vane applications. To allow for formation of an $Y_2O_3$ dispersion, 0.2 Y weight percent was included in the alloy. The SAP technique,[*] in which an oxide dispersion is formed by partial oxidation of metal powders before consolidation, was used to prepare an oxide dispersion strengthened NiCrAl because of the simplicity of this method, and because the SAP technique had not previously been applied to a NiCrAl alloy.

The portion of the total study (ref. 1) reported herein describes application of the SAP technique to a NiCrAlY alloy, the oxide dispersion obtained, and the recrystallization processes occurring in the consolidated and worked product. Because oxidation removed yttrium from the NiCrAlY alloy, the product prepared from the oxidized powder is referred to as SAP-NiCrAl; the product prepared from unoxidized NiCrAlY retained its yttrium and is termed unoxidized NiCrAlY in this report.

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[*]An acronym for Sintered Aluminum Powder in which a naturally occurring oxide, as opposed to a blended-in oxide, is used for oxide dispersion strengthening.

## MATERIALS AND EXPERIMENTAL PROCEDURE

### Powder Preparation

A nickel alloy containing 17 percent chromium, 5 percent aluminum, and 0.2 percent yttrium was used in this study. The alloy was produced as prealloyed powder by argon gas atomization. Only minus 325 mesh (less than 44 μm diameter) powder was used. The alloy powder average size indicated by use of the Fisher Sub-Sieve Sizer was 20 μm. An oxide distribution was produced by the SAP technique, that is, partial oxidation of metal powder prior to consolidation. The technique has been previously applied to FeCrAl alloys (refs. 13-15). The powder was oxidized at 630° C in air in a shallow (1/2 cm) bed, removed after 1 hour of oxidation, sieved through a 100 mesh screen to break up any agglomerates, blended, and then similarly oxidized for an additional hour.

The oxidized powders were examined by optical and scanning electron microscopy. To examine the oxide alone, carbon surface extraction replicas were prepared by carbon coating the oxidized pow . .nd dissolving the underlying metal slowly in 2 percent bromine in ethanol. The oxide particles attached to the carbon-coated remaining shell were viewed by transmission electron microscopy. To identify the oxides present, electron diffraction patterns of the oxide particles were obtained.

### Thermomechanical Processing Treatments

_Working_. - Oxidized and, for comparison, unoxidized powders were packed using vibration into 304 stainless steel extrusion cans. The cans were 9.6 centimeters in diameter and 19 centimeters in length with a wall thickness of 1.2 centimeters. The extrusion cans were sealed under vacuum at 260° C by electron beam welding. The powder filled cans were

reduced 16:1 (94 percent in area) by extrusion at 1205° C. Following extrusion, additional working was accomplished by rod rolling at 1205° C (for a reduction in area in six passes of approximately 67 percent). After rod rolling, specimens were reduced approximately 18 percent in area in each of two swaging passes at 760° C. Single specimens given one and three swaging reductions of 18 percent in area per pass were also produced but unless otherwise stated, swaged materials discussed in this report are those that received two swaging reductions. The specimens were reheated to the working temperature between working passes in both rod rolling and swaging operations, but were not annealed at more elevated temperatures until working was complete. All working and annealing steps were performed without removal of the stainless steel extrusion cans.

Annealing. - The annealing specimens were cylinders of approximately equal length and diameter (about 1 cm for swaged specimens). The NiCrAl portion of such specimens was about 0.5 centimeter in diameter, the surrounding metal being the stainless steel can residual from extrusion. All samples were annealed in air and then cooled in air.

The various annealing treatments are summarized in table I. These treatments were designed to provide a comparison between unoxidized NiCrAlY and SAP-NiCrAl and, in the case of swaged SAP-NiCrAl to determine the microstructural response to annealing time and temperature. Anneals were also performed to determine the effects of amount of swaging reduction and specimen geometry on SAP-NiCrAl.

Preferred orientation. - Because of a dichotomy of recrystallization response observed in SAP-NiCrAl specimens given two swaging reductions, two samples, one representing the central (axial) portion, and the other

the annular portion of the specimen, were prepared by machining. The crystallographic texture of each portion was determined by x-ray diffraction.

### Microstructural and Chemical Examinations

Composition. - The composition of SAP-NiCrAl was determined after oxidation of the powder and after complete processing including extrusion, rod rolling, swaging and a one-hour anneal at $1340^{\circ}$ C. The metal concentrations were determined by wet chemical analysis while the oxygen content was determined by inert gas fusion analysis. Oxides were extracted from SAP-NiCrAl after extrusion using a solvent of 10 percent bromine in methanol; the extracted oxides were examined by x-ray diffraction to determine their identity.

Microstructural examination. - Longitudinal and transverse samples in the various as-worked and as-annealed conditions were examined metallographically. These samples were etched electrolytically with an etchant consisting of 33 percent water, 33 percent nitric acid, 33 percent acetic acid, and 1 percent hydrofluoric acid.

For measurements of grain size, the Heyn intercept procedure (ref. 16) was used. Lines sufficiently long to intercept about 150 grains were used. Because of the cylindrical symmetry of the samples, grains were counted in only the longitudinal (axial) and one transverse direction. To calculate the number of grains per cubic millimeter, $n_v$, the following equation was used: $n_v = 0.7\ n_1 n_t^2$, where $n_1$ is the number of grain interceptions per millimeter in the longitudinal direction and $n_t$ the number in the transverse direction. Following ASTM practice (ref. 16), the corresponding equiaxed grain size was calculated from the number of

grains per cubic millimeter. All grain sizes reported in the body of this paper refer to the calculated equiaxed grain size. In table II grain lengths and widths are included in addition to the calculated grain size.

## RESULTS AND DISCUSSION

### Characterization of the Oxide Dispersion

No differences between unoxidized and oxidized NiCrAlY powders were observed by optical microscopy. Powders are here called NiCrAlY (figs. 2 to 4) even though oxidized because Y is still in the alloy, not in the oxide. However, some differences were discerned by scanning electron microscopy. As may be seen in figure 1, the as-received powders appeared smooth and clean. Surface relief caused by solidification shrinkage in interdendritic areas could be detected on large powder particles. Oxidized powders, shown in figure 2, exhibited some flakes, presumably oxides, frequently lying along the interdendritic zones.

To identify the oxides present on the surface of the oxidized powders and the general oxide morphology, carbon surface extraction replicas were prepared and examined by transmission electron microscopy. Thin spherical shells with thicker portions presumably formed at the interdendritic areas can be seen in figure 3. At very high magnification, distinct oxide particles 300 to 1000 $\overset{o}{A}$ in width and approximately 100 $\overset{o}{A}$ thick were resolved lying in or on the thin carbon shells (fig. 4). The primary oxide component was identified as NiO by electron diffraction.

While the primary oxide present on the oxidized powder particles was NiO, oxides extracted from extruded SAP-NiCrAl were found by x-ray diffraction to be $Y_2O_3$ and $Al_2O_3$. It is apparent that during the time at

$1205^\circ$ C required for heat up and extrusion, Y and Al in the alloy reduced the NiO. The oxides were examined in situ by scanning electron microscopy; particles high in either Al or Y were observed.

The oxygen content of extruded SAP-NiCrAl was determined by inert gas fusion analysis. The two-hour, $630^\circ$ C oxidation treatment applied to NiCrAlY powder increased the oxygen content from 96 ppm in the as-received powder to 2400 ppm.

The volume percent of oxide in the extruded SAP-NiCrAl was calculated using the following assumptions: All oxygen in the material formed either $Y_2O_3$ or $Al_2O_3$ and $Y_2O_3$ formed in preference to $Al_2O_3$ until all the yttrium in the matrix was consumed. The calculated oxide volume percent was 1 percent with about equal amounts of $Y_2O_3$ and $Al_2O_3$. In comparison the calculated volume percent of oxide in unoxidized NiCrAlY was about 0.04 percent and was considered negligible. No change in chemical composition other than the change in oxygen content was detected. The alloy's composition was 16.8 Cr, 4.9 Al, 0.2 Y and balance nickel.

As illustrated in figure 5, the oxides in extruded SAP-NiCrAl were found to lie in narrow bands corresponding to the prior particle boundaries. They were blocky in form, and ranged from 0.1 to 1 µm in size. Their average size was about 0.3 µm. Interparticle spacings within a band were on the order of 1 µm, while the parallel bands were from 1 to 10 µm apart. The microstructure of unoxidized extruded NiCrAlY, shown in figure 6, exhibits far fewer oxide particles. This is consistent with its much lower calculated oxide content.

From these results it may be concluded that the technique of preoxidation of metal powders used in this study does not produce oxides suffi-

ciently fine or well dispersed to be considered appropriate for disper-
sion strengthening. The NiO which formed during oxidation was of fine
size; but in the reduction of the NiO and formation of $Y_2O_3$ and $Al_2O_3$
large particles were formed. A similar judgment was reached in the
application of the SAP process to FeCrAl alloys (ref. 17).

Only a slight strengthening effect of the oxide dispersion was
noted when unoxidized NiCrAlY and SAP-NiCrAl of comparable grain struc-
ture were tested in tension. For example at 1095° C SAP-NiCrAl exhibited
an ultimate tensile strength of 30 $MN/m^2$ compared to a value of 23 $MN/m^2$
for unoxidized NiCrAlY (ref. 1).

### Annealing Response

Microstructures of experimental products were characterized pri-
marily by their grain size and shape. The dimensions of grains for
various conditions are given in table II in terms of average grain length
and grain width, the length-to-diameter ratio also referred to as grain
aspect ratio (GAR), and the corresponding equiaxed grain size.

Unoxidized NiCrAlY. - Worked unoxidized NiCrAlY such as that shown
in figure 7 exhibited somewhat irregular grain boundaries. As can be
noted from table II, annealing at 1340° C for one hour after any of the
working treatments (extrusion, rod rolling, or swaging) substantially
increased the grain size of unoxidized NiCrAlY. After anneal, the micro-
structures of unoxidized NiCrAlY, such as that shown in figure 8, were
quite similar to each other except in grain size. During anneal the
grain boundaries became much smoother and approached equilibrium shapes.
No evidence of abnormal grain growth was observed in annealed unoxidized
NiCrAlY after any of the working treatments.

SAP-NiCrAl. - As worked SAP-NiCrAl, an example of which is shown in figure 9, exhibited grains similar to worked unoxidized NiCrAlY (fig. 7) in grain boundary irregularity but were generally somewhat smaller and more elongated. The annealing response of SAP-NiCrAl was quite different from unoxidized NiCrAlY as may be noted from table II. Annealing SAP-NiCrAl after extrusion or rod rolling did not result in any substantial increase in grain size. The grain size achieved on annealing after extrusion or rod rolling (fig. 10) was not limited to the distance between prior powder particle boundaries as is often the case in extruded powder metallurgy superalloys (ref. 18). The grain boundaries were evidently affected by the presence of oxide particles, however, because the boundaries were much more irregular than in the oxide free product (compare fig. 10 to fig. 8).

Swaged SAP-NiCrAl exhibited both very small (14 μm) and very large (1000+ μm) grains after anneal (table II and fig. 11). These grains appeared to be the result of abnormal grain growth. Because very large grains were observed in the swaged product, concentrated attention was given to both the swaged unoxidized NiCrAlY and the swaged SAP-NiCrAl. Unless otherwise stated, swaged materials discussed are those subjected to two swaging passes after rod rolling.

Effect of annealing temperature. - Qualitative observations of response to annealing at temperatures ranging from 760° to 1340° C (~55° C intervals) of swaged unoxidized NiCrAlY and SAP-NiCrAl are listed in table III. Briefly, both swaged unoxidized NiCrAlY and SAP-NiCrAl resisted recrystallization at 925° C or lower. Recrystallization from somewhat elongated to fine equiaxed grains was noted for SAP-NiCrAl after one hour

at 980° C and for unoxidized NiCrAlY after one hour at 1040° C. As annealing temperature increased above these temperatures, the resultant grain size increased. However, the grain size in SAP-NiCrAl after annealing at temperatures below 1340° C was consistently much smaller than that in unoxidized NiCrAlY. At the highest temperature of anneal, 1340° C, swaged unoxidized NiCrAlY exhibited uniformly large grains (107 μm) similar to those formed at lower annealing temperatures. Swaged SAP-NiCrAl after anneal at 1340° C exhibited fine grains (14 μm) similar to those formed at lower temperature, but in addition, coarse grains more than 1000 μm in diameter were observed (fig. 11).

Thus, only normal recrystallization and grain growth were observed for unoxidized NiCrAlY at all temperatures and for SAP-NiCrAl annealed below 1340° C. But grains resulting from abnormal recrystallization were observed after normal recrystallization upon annealing swaged SAP-NiCrAl at 1340° C.

In a second series of anneals (listed in table I) also conducted to determine the effect of annealing temperature on swaged SAP-NiCrAl, it was observed that abnormal recrystallization did not occur at temperatures of 1255°, 1275°, 1295°, and 1310° C but did occur at 1325° and 1340° C. The existence of a minimum temperature below which response will not occur is consistent with observations of abnormal grain growth (ref. 11).

Effect of annealing time on swaged SAP-NiCrAl. - Samples of swaged SAP-NiCrAl were annealed at 1095°, 1205°, and 1340° C for times ranging from one minute to 24 hours. The resulting grain sizes are given in table IV.

At all three temperatures complete recrystallization from 21 μm, as

swaged, elongated grains to equiaxed grains of about 10 μm diameter occurred in less than 4 minutes. Normal grain growth was first observed after 60 minutes at 1095° and 1205° C and after 2 minutes at 1340° C. Growth was slow for all three temperatures of anneal. The largest grain size obtained after 24 hours (1440 min) at 1095° C was 14 μm. This size (interpolated) was attained after 3 hours at 1205° C. In the annular normal grain growth portion of samples annealed at 1340° C, 14 μm diameter grains were observed after only 8 minutes.

The specimen of swaged SAP-NiCrAl annealed at 1205° C for 16 minutes is shown in figure 12. The fine equiaxed grains derived by primary recrystallization of this specimen were typical of grains observed in all swaged SAP-NiCrAl annealed at 1095° or 1205° C. They were also typical of the fine grains derived by primary recrystallization during anneal at 1340° C. Grains having linear dimensions of more than three times the average grain size were apparent in every specimen which had recrystallized to fine grain size during annealing. These grains were uniformly distributed and there was no gradient of grain size from the center to the annular portion of primary recrystallized swaged SAP-NiCrAl.

Very large grains of 1000 μm diameter were observed in specimens annealed 2 minutes or more at 1340° C. The specimen annealed for 1 minute at 1340° C (fig. 13) had undergone complete primary recrystallization to fine grains. However, one grain much larger than the rest had already developed. It is apparent from figure 13 that this grain grew at the expense of at least 1000 other grains.

After 2 minutes at 1340° C, formation of the very large grains was complete, though only part of the specimen volume was consumed. The cen-

tral one third of the SAP-NiCrAl specimen transformed while the annular two thirds remained fine grained. The volume of the specimen consumed by very large grains did not increase with time after two minutes; nor were fine grains within the large grains completely eliminated after 24 hours at 1340° C.

Although the annealing temperatures 1095° and 1205° C are well above the gamma prime solvus for the alloy studied (ref. 19), abnormal grain growth did not occur at these temperatures. This is in contrast to observations in the superalloy 713-C in which the progress of abnormal recrystallization was dependent upon the dissolution of gamma prime (ref. 20).

From the very slow normal grain growth exhibited even at 1340° C, it may be concluded that the oxides present, though not stopping it completely, do hinder normal grain growth. The doubling of SAP-NiCrAl grain size from 10 to 19 μm in 1440 minutes at 1340° C (table IV) may be contrasted to the tripling of grain size in oxide free NiCrAlY from 32 to 107 μm in 60 minutes at 1340° C (table III).

Effect of preannealing on swaged SAP-NiCrAl. - It was found that the processes of formation of fine and of coarse grains could be separated by annealing first at one temperature (e.g., 1095° or 1205° C) to cause recrystallization to fine grains (10 or 11 μm) and later at a higher temperature (1340° C) to produce abnormal grains. The microstructure of such preannealed samples exhibited the same growth of large grains after 1340° C anneal as specimens which had been annealed only at 1340° C. The large grains were limited to the central (axial) portion of the specimens. This same dichotomy of recrystallization response was observed in all

swaged (2 pass) SAP-NiCrAl after anneal at 1340° C.

Even in the case of the specimen annealed first 12 hours at 1205° C, then heated slowly to 1340° C, large grains were formed. The time at 1205° C and the slow heating to 1340° C were considered sufficient to eliminate any stored energy (for example, from differential thermal expansion), other than that associated with grain boundaries.

These two-step annealing treatments, more clearly than single step anneals, provided a definite separation between the processes of primary and secondary (abnormal) recrystallization. And the achievement of very large grains in slow heating from 1205° to 1340° C is consistent with the usual consideration that grain boundary energy provides the driving force for secondary recrystallization (ref. 11).

Cause of dichotomy of recrystallization response in swaged SAP-NiCrAl. - As mentioned above, swaged SAP-NiCrAl after 1340° C anneal exhibited two distinctly different patterns of recrystallization. The central (axial) area of specimens underwent both primary and secondary recrystallization to form coarse grains. In the outer (annular) portion only primary recrystallization to fine grains occurred. To determine the cause of this difference several features of swaged SAP-NiCrAl and its response to annealing were examined. These included the crystallographic texture of the axial and annular portions of swaged (2 pass) SAP-NiCrAl, the degree of swaging reduction prior to anneal, the grain size in the axial and annular portions after primary recrystallization, the extent of diffusion between the SAP-NiCrAl and the stainless steel can, and the geometry of the specimen used for anneal.

Amount of working: The area (annular portion) in swaged SAP-NiCrAl

in which fine grains would form on annealing was found to have a [111] fiber texture. The area in which coarse grains would form was found to have a dual fiber texture of [111] and [100]. This texture difference suggested the possibility of unequal amounts of deformation in the two areas. To check this possibility, samples of SAP-NiCrAl were swaged using one or three passes instead of the usual two passes. After 1 hour $1340^\circ$ C anneal the one pass sample exhibited only fine grains; in the sample swaged using three passes, abnormal recrystallization to coarse grains proceeded across essentially the entire specimen. While this indicated that unequal working contributed to the varying textures and recrystallization response, a more extensive study of textures would be required for complete confirmation.

Other factors: The other factors which were examined did not appear to contribute to the dichotomy of recrystallization response. The average grain size after primary recrystallization was determined for positions in the axial and annular portions of swaged SAP-NiCrAl. No gradient in grain size from specimen interior to exterior was found. The diffusional interaction with the stainless steel can was found to be slight by chemical analysis of SAP-NiCrAl before and after complete processing including one hour $1340^\circ$ C anneal. Nor did the usual cylindrical specimen shape contribute to the recrystallization difference. A specimen of swaged SAP-NiCrAl was sectioned along its longitudinal axis prior to annealing 30 minutes at $1340^\circ$ C. The spatial distribution of fine and coarse grains was the same as in specimens sectioned after anneal.

### Results in Terms of Zener-Hillert Concept

The above results showed that the recrystallization processes in

swaged SAP-NiCrAl occurred in two distinct and separable steps. These steps were normal recrystallization to fine equiaxed grains and then secondary recrystallization to fewer but much larger grains. After the step of primary recrystallization, the swaged SAP-NiCrAl met the three prerequisites for secondary recrystallization given by Hillert (ref. 21) following the thoughts of Zener.

These three prerequisites are (1) normal grain growth cannot take place because of the presence of second phase particles, (2) the average grain size after primary recrystallization lies below the limit, ~0.5 d/f where  d  is the particle diameter and  f  is the volume fraction of second phase, and (3) there is at least one grain much larger than the average.

Normal grain growth was inhibited by the presence of dispersoid particles. While not stopped completely, the grain size attained by fine grains in swaged SAP-NiCrAl after 1 hour of anneal at 1340$^\circ$ C was 14 μm; for NiCrAl similarly worked, but not containing oxide dispersoids, the grain size after 1 hour of anneal at 1340$^\circ$ C was 74 μm.

The average grain size of swaged SAP-NiCrAl after primary recrystallization was below the limit 0.5 d/f. In swaged SAP-NiCrAl prior to annealing the average particle diameter was about 0.3 μm; the volume fraction was 0.01. The grain size limit was thus 0.5 × 0.3 μm × $10^2$, or approximately 15 μm. This compares to the grain size 10 μm observed after one minute of anneal at 1340$^\circ$ C.

The third requirement, the presence of at least one grain substantially larger than the average, was consistently met in swaged SAP-NiCrAl specimens after primary recrystallization.

These results are analogous to those obtained in the studies of TD-Ni (ref. 9) and TD-NiCr (ref. 10). There was, however, a notable difference: The dispersions characteristic of TD-Ni and TD-NiCr were much finer than the oxide distribution observed in SAP-NiCrAl. This led for example, to a limiting grain size before secondary recrystallization imposed by the Zener-Hillert 0.5 d/f requirement of about 2 μm for TD-Ni compared to about 15 μm for SAP-NiCrAl. Despite this almost order of magnitude difference, the same requirements governing secondary recrystallization for TD-Ni appear also to apply in the case of SAP-NiCrAl.

## CONCLUDING REMARKS

Perhaps the most significant feature of this investigation is the finding that the Zener-Hillert requirements for secondary recrystallization appear to be applicable even in the case of a large size and poorly distributed dispersion of second phase particles. Thus a dispersion of oxide particles considered too coarse to have a significantly beneficial effect on an alloy's strength might nonetheless be introduced as an aid to control recrystallization behavior. For example, secondary recrystallization to large grains might be obtainable in some superalloys through inhibition of normal grain growth by a dispersion of oxide particles. A coarse oxide dispersion such as examined in this investigation is readily obtainable by powder metallurgical techniques.

An application of this concept could be in the area of powder metallurgy alloys of high gamma-prime content in which grain growth is difficult. Such alloys are receiving attention for gas turbine disk applications at intermediate temperatures (650° to 750° C). However, they could be potential turbine blade alloys if higher stress rupture strengths asso-

ciated with larger grain sizes were achievable. By the use of dispersed oxides, secondary recrystallization might be induced in such alloys to yield large grain sizes. The attainment of large grain size has been shown in other studies to improve the stress rupture life of superalloys made by powder metallurgy techniques (ref. 18).

A possible method of improving the SAP process employed in this study might be to form the aluminum or yttrium oxides directly on or in the powder without first forming NiO. For example, Pettit lists conditions of alloy composition, temperature, and oxygen activity for which oxidation of aluminum will occur without the formation of NiO (ref. 22). Some improvement might also be derived by the use of splat cooled powders in which the initial distribution of the Y would be expected to be superior to that in atomized powders.

## SUMMARY AND CONCLUSIONS

Investigation of the application of the SAP process to a NiCrAl alloy and its recrystallization response has produced the following results and conclusions.

1. The process of preoxidation of Ni–17Cr–5.5 Al–0.2 Y powder in air at 630° C applied in this study produces fine NiO oxide particles. During processing these NiO particles are reduced by Y and Al from the alloy forming a coarse and widely spaced oxide dispersion of $Y_2O_3$ and $Al_2O_3$.

2. The annealing response of unoxidized NiCrAlY after hot extrusion, hot rolling, or warm swaging is normal recrystallization.

3. The annealing response of SAP–NiCrAl after hot extrusion or hot rolling is normal recrystallization. However, after warm swaging a two-step process of primary followed by secondary (abnormal) recrystallization occurs.

4. Although the oxide size and spacing in SAP-NiCrAl are an order of
magnitude greater than in TD-Ni or TD-NiCr the same relation between pri-
mary recrystallization grain size, dispersoid parameters, and occurrence
of abnormal recrystallization was observed.

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TABLE I. - SUMMARY OF ANNEALING TREATMENTS APPLIED TO UNOXIDIZED NiCrAlY AND SAP-NiCrAl

| Material | Working history[a] | Preanneal Temperature, °C | Preanneal Time, min | Anneal Temperature, °C | Anneal Time, min |
|---|---|---|---|---|---|
| Unoxidized NiCrAlY and SAP-NiCrAl | Extruded, extruded and rod rolled, extruded, rod rolled, and swaged (2 passes) | | | 1340 | 60 |
| Unoxidized NiCrAlY and SAP-NiCrAl | Extruded, rod rolled, and swaged (2 passes) | | | 760 to 1340 | 60 |
| SAP-NiCrAl | Extruded, rod rolled, and swaged (2 passes) | | | 1095 | 1 to 1440 |
| | | | | 1205 | 1 to 1440 |
| | | | | 1340 | 1 to 1440 |
| | | | | 1255 | 20 |
| | | | | 1275 | 20 |
| | | | | 1295 | 20 |
| | | | | 1310 | 20 |
| | | | | 1325 | 20 |
| | | | | 1340 | 20 |
| | | 1095 | 30 | 1340 | 60 |
| | | 1205 | 30 | 1340 | 60 |
| | | 1205 | 720 | 1340 | 60 |
| SAP-NiCrAl | Extruded, rod rolled and swaged (1 pass) | | | 1340 | 60 |
| SAP-NiCrAl | Extruded, rod rolled and swaged (3 passes) | | | 1340 | 60 |

[a]Note that working was cumulative; extrusion followed by rod rolling followed by swaging.

TABLE II. – GRAIN SIZE AND SHAPE OF UNOXIDIZED NiCrAlY AND

SAP-NiCrAl AFTER THERMOMECHANICAL PROCESSING

| Thermomechanical processing history[a] | Grain length, μm | Grain width, μm | Grain aspect ratio | Average diameter, μm |
|---|---|---|---|---|
| Unoxidized NiCrAlY | | | | |
| Extruded | 12 | 13 | 0.9 | 14 |
| Extruded and annealed[b] | 121 | 108 | 1.1 | 127 |
| Extruded and rod rolled | 51 | 48 | 1 | 55 |
| Extruded, rod rolled and annealed | 300 | 400 | 0.75 | 400 |
| Extruded, rod rolled and swaged | 37 | 24 | 1.5 | 32 |
| Extruded, rod rolled, swaged and annealed | 65 | 29 | 1 | 74 |
| SAP-NiCrAl | | | | |
| Extruded | 28 | 18 | 1.5 | 23 |
| Extruded and annealed | 19 | 16 | 1.2 | 19 |
| Extruded and rod rolled | 26 | 18 | 1.4 | 23 |
| Extruded, rod rolled and annealed | 36 | 28 | 1.3 | 34 |
| Extruded, rod rolled and swaged | 31 | 15 | 2 | 22 |
| Extruded, rod rolled,   Primary swaged and   Secondary annealed | 12 1000+ | 13 1000+ | 0.9 ~1 | 14 1000+ |

[a]Note that working was cumulative; extrusion followed by rod rolling followed by swaging.

[b]All anneals 1 hour at 1340° F.

[c]This treatment produced a mixed structure part of which resulted from primary recrystallization alone and part from primary followed by secondary (abnormal) recrystallization.

TABLE III. - MICROSTRUCTURES OF SWAGED UNOXIDIZED NiCrAlY

AND SWAGED SAP-NiCrAl AFTER ONE HOUR ANNEAL

| Annealing temperature, °C | Grain size[a] and shape[b] | |
|---|---|---|
| | Unoxidized NiCrAlY | SAP-NiCrAl |
| 760 | As swaged, 32 μm, GAR = 1.5 | As swaged, 21 μm, GAR = 2 |
| 815 | | |
| 870 | | No recrystallization |
| 925 | No recrystallization | |
| 980 | | Recrystallized, 8 μm, GAR = 1 |
| 1040 | Recrystallized, 21 μm, GAR = 1 | |
| 1095 | | |
| 1150 | Increasing grain size | Increasing grain size |
| 1205 | | |
| 1260 | | |
| 1340 | Recrystallized, 107 μm, GAR = 1 | Abnormal recrystallization mixed, 14 μm and 1000+ μm, GAR = 1 |

[a]Size given is calculated diameter of average grain.

[b]Shape given is the grain aspect ratio, GAR, the ratio of grain length to width.

TABLE IV. - GRAIN SIZE OF SWAGED SAP-NiCrAl AFTER

ANNEAL AT 1095°, 1205°, OR 1340° C

| Duration of anneal, min | Average grain diameter in μm after annealing | | | |
|---|---|---|---|---|
| | At 1095° C, p[a] | At 1205° C, p[a] | At 1340° C | |
| | | | p[a] | s[b] |
| 0 | 21 | 21 | 21 | 21 |
| 1 | 24 | 12 | 10 | 200 |
| 2 | 13 | 11 | 11 | 1000+ |
| 4 | 10 | 10 | 12 | 1000+ |
| 8 | 10 | 10 | 14 | 1000+ |
| 16 | 10 | 10 | 14 | 1000+ |
| 30 | 9 | 10 | 14 | 1000+ |
| 60 | 11 | 11 | 14 | 1000+ |
| 120 | 12 | 12 | n.d. | 1000+ |
| 240 | 14 | 16 | n.d. | 1000+ |
| 1440 | 14 | 19 | 19 | 1000+ |

[a]Grains formed by primary recrystallization.

[b]Grains formed by secondary (abnormal) recrystallization.

n.d.Not determined.
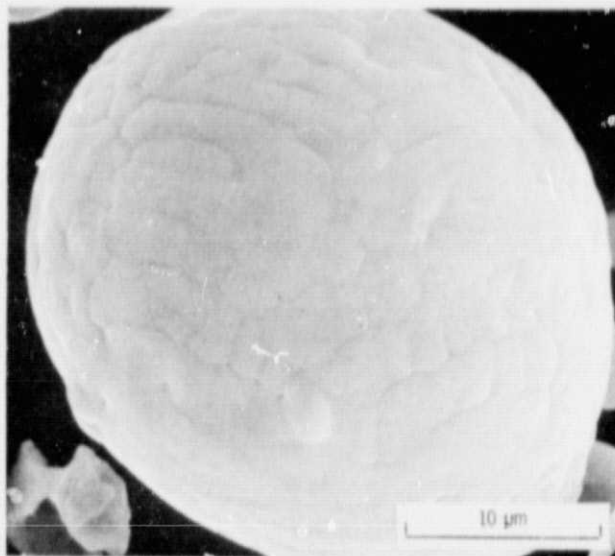
Figure 1. – Scanning electron microscope photograph of as-received NiCrAlY powder. X3000.
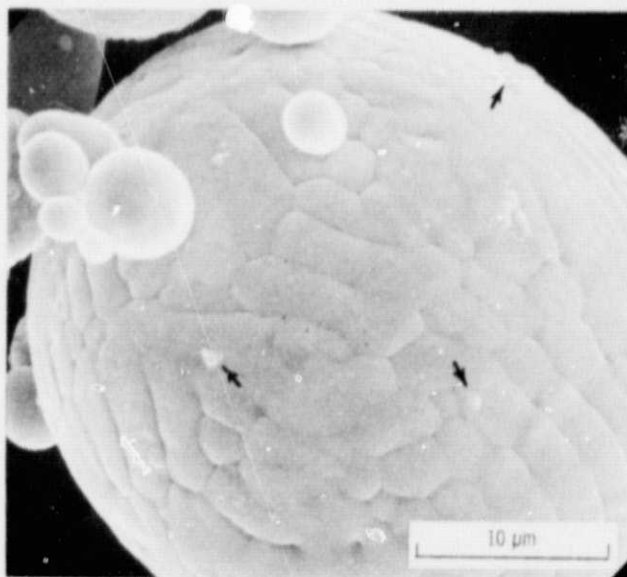


Figure 2. – Scanning electron microscope photograph of oxidized NiCrAlY powder. X3000. Note the presence of oxide flakes on the powder surface (arrows).

Figure 4. – Transmission electron microscopy photograph of a carbon surface extraction replica of oxidized NiCrAlY powder. X90 000.

1 μm



Figure 3. – Transmission electron microscopy photograph of a carbon surface extraction replica of oxidized NiCrAlY powder. X11 000.

5 μm
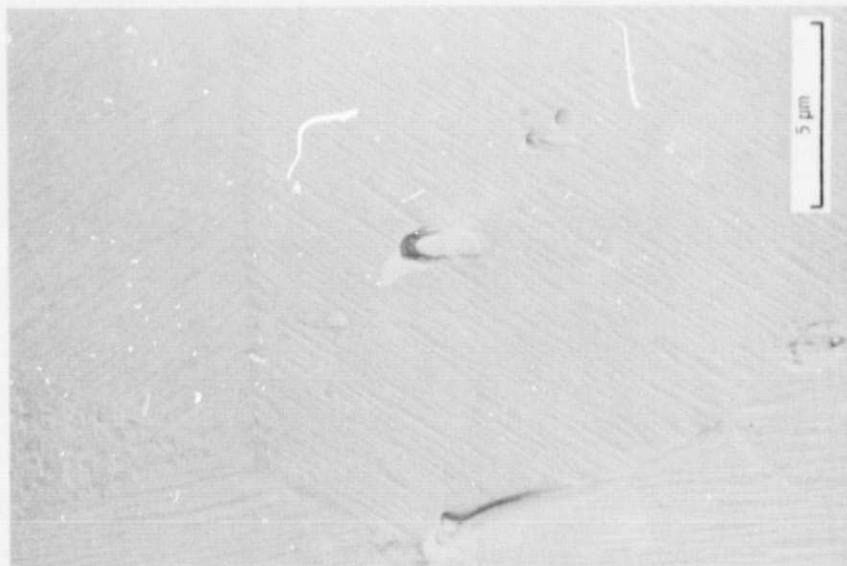
Figure 6. - Microstructure of as-extruded unoxidized NiCrAlY. X10 000. Note the very straight grain boundaries.
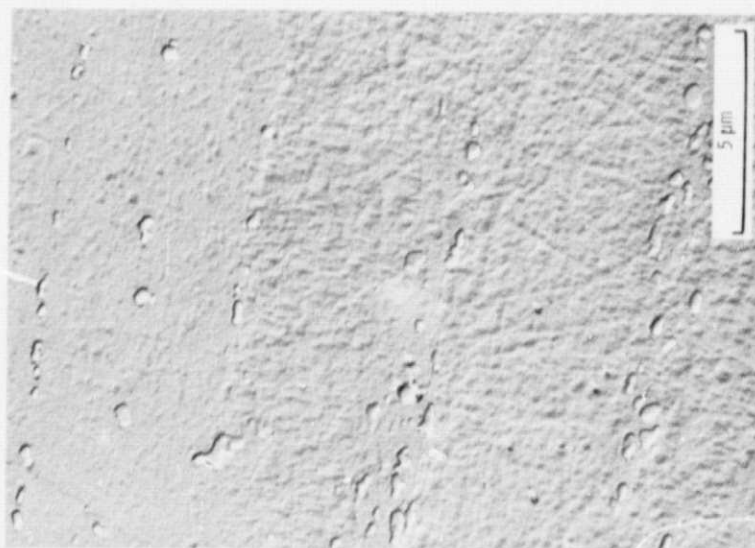


Figure 5. - Oxide distribution in as-extruded SAP-NiCrAl. X11 000.
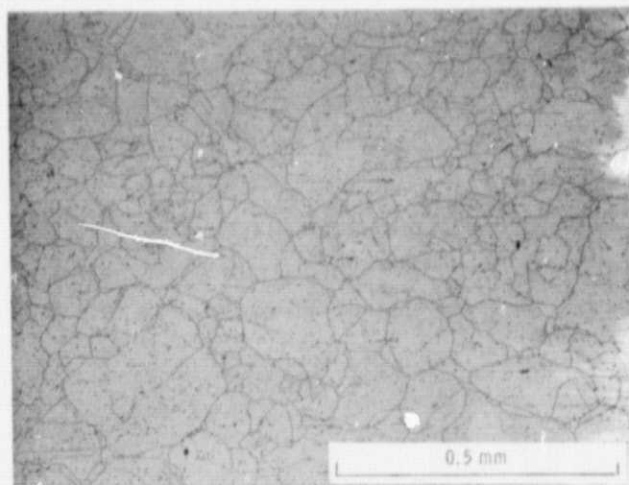
Figure 7. - Extruded and rod rolled unoxidized NiCrAlY, typical of the as-worked condition. X100.
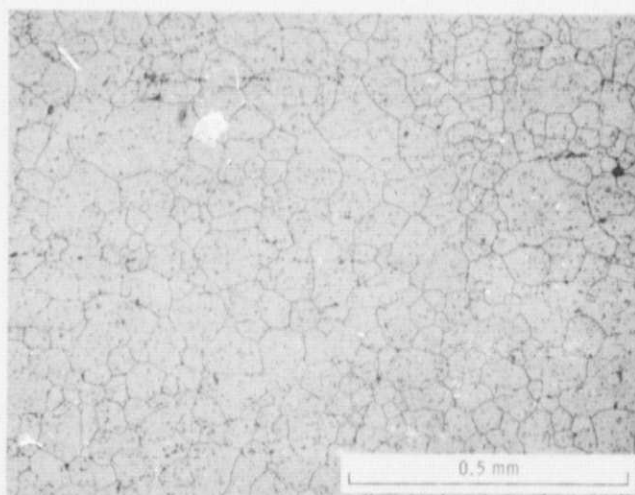


Figure 8. - Extruded, rod rolled, swaged, and annealed (one hour, 1260° C) unoxidized NiCrAlY, typical of annealed unoxidized NiCrAlY. X100.
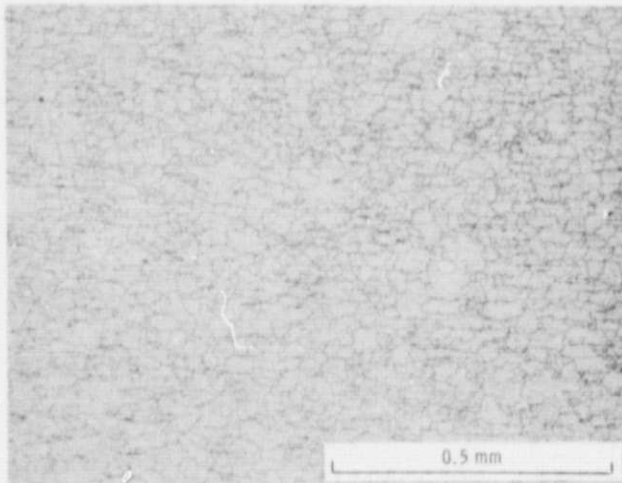
Figure 9. - Extruded SAP-NiCrAl, typical of as-worked SAP-NiCrAl.
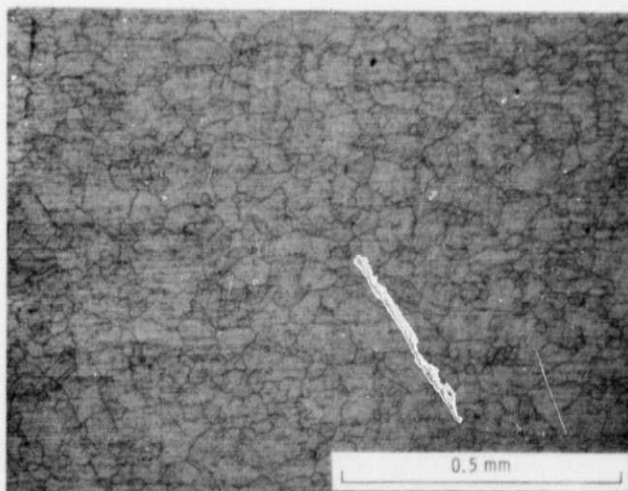
Figure 10. - Extruded, rod rolled, and annealed (one hour, 1340° C) SAP-NiCrAl which did not exhibit abnormal (secondary) grain growth. X100.
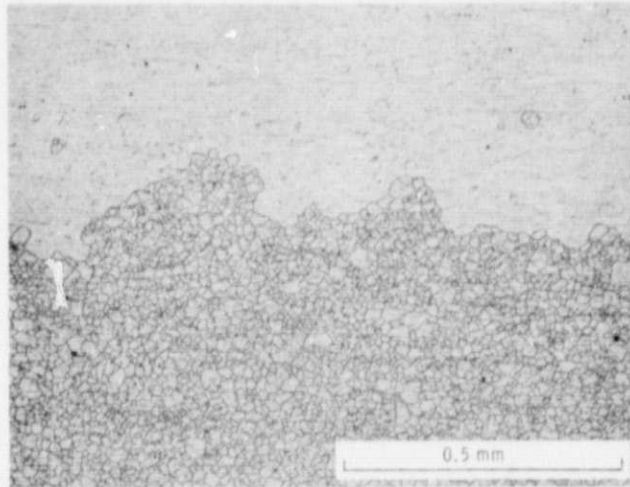
Figure 11. - Extruded, rod rolled, and swaged SAP-NiCrAl after (one hour, 1340° C) anneal showing a portion of one large (secondary) grain and numerous fine (primary) grains. X100.
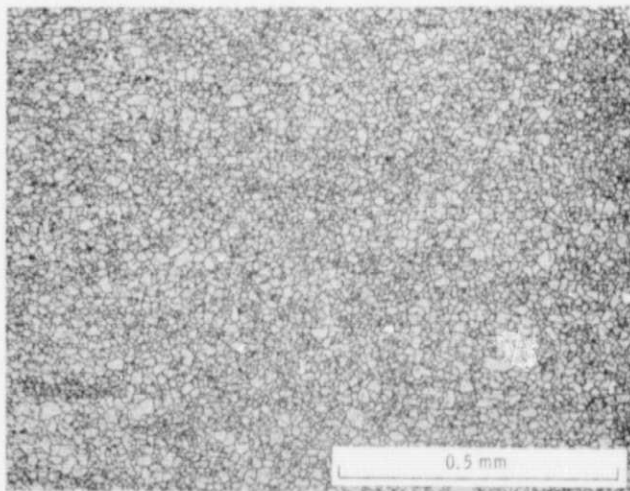


Figure 12. - Extruded, rod rolled, and swaged SAP-NiCrAl, annealed 16 minutes at 1205° C, typical of swaged SAP-NiCrAl samples after primary recrystallization. X100.
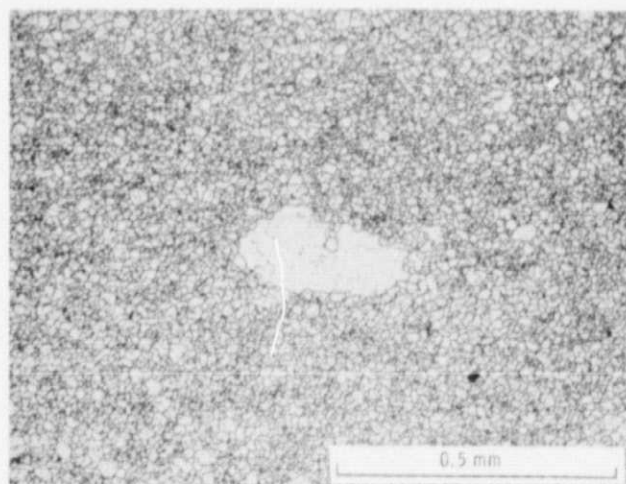
0.5 mm

Figure 13. - Extruded, rod rolled, and swaged SAP-NiCrAl after one minute
anneal at 1340⁰ C.  Primary recrystallization was complete and secondary
(abnormal) recrystallization had begun.  (Note one secondary grain.)