ON THE CELESTIAL LIMITS OF NICKEL-BASE SUPERALLOYS

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Introduction

Nickel-base superalloys have been under continuous development for many decades. As reflected by the interests of the present symposium, the current emphasis is on improvements through processing. In order not to beat the proverbial horse to death, it may prove prudent at this time to obtain estimates on some of the remaining potentials of nickel-base superalloys. In other words, what are some of the upper or celestial limits of the mechanical properties of nickel-base superalloys? Have we already reached them? And, if not, is processing the means to get there? We believe that the science of nickel-base superalloys is now sufficiently well developed so that these questions can be answered in a fairly painless manner. In what follows, we choose to discuss the three properties of major concern in gas turbine applications; yield strength, creep and fatigue.

Yield Strength

This of course is one of the more fundamental properties of a structural alloy. It is a property to be maximized, and, in the case of elevated temperature applications to be made invariant with temperature. Nickel-base superalloys are super because they possess reasonable strength to reasonably high temperatures, as a consequence of strengthening by such ordered and coherent particles as γ' [$Ni_3(Al,X)$]. Naturally, we greed for more. Let us now examine the feasibility of achieving more. Forgetting about grain boundaries for the moment, let us first discuss the strength of single crystals of nickel-base superalloys (intragranular strength).

The understanding of the strengthening mechanism of γ' particles is in a very interesting state of development. As a consequence of complications resulting from dislocations bowing between, as well as cutting through the coherent γ' particles, the strengthening mechanism of γ' in alloys where the γ' volume fraction is academically low is not well understood. However, when the volume fraction is high and particles are fine in size, the particles are essentially stringed together and can be looked upon as a continuous array; dislocation cutting of particles then becomes the only consideration. In this case, which is also the case of practical interest because contemporary high strength nickel-base superalloys are well endowed with γ' particles (50% or greater is not unusual), Fig. 1, the physically elegant strengthening theory of Copley and Kear [1] applies. Let us apply it to the yield strength versus temperature data shown in Fig. 2.

In Fig. 2, the bottom curve corresponds to the yield strength (given as critical resolved shear stress) of an alloy (Udimet-700) strengthened by the familiar distribution of γ' cuboids, Fig. 1a or 1b, the middle curve corresponds to the yield strength of the same alloy after a compressive stress anneal to produce the aligned rods, Fig. 1c, and the top curve corresponds to the yield strength of the same alloy after a tensile stress anneal to produce the broad γ' plates, Fig. 1d. It should also be mentioned that stress annealing, which is essentially annealing under small loads, will cause the alloy to undergo primary creep and thus result in dislocation networks, Fig. 3, about the particles, whose role in creep will be discussed later. The details involving Figs. 1-3 are reported elsewhere.[2] For the purpose of this paper we use these figures in conjunction with the theory of Copley and Kear to illustrate certain limiting conditions.

Firstly, regardless of γ' morphology, the yield strength of nickel-base superalloy drops fairly abruptly at about 1400°F (the knees of the curves in Fig. 2). This finding is consistent with what can best be described as a decrease in the degree of ordering in the γ' particles and the associated sharp decrease in Antiphase Boundary (APB) Energy*,

which is the dominant restraining force to dislocation motion during yielding. [1] Above 1400°F the location of the strength-temperature knee is also observed to depend on strain rate, with the knee moving to higher temperatures as strain rate is increased.[3] This strain rate dependence strongly indicate that the disordering process in γ' is caused by the intruding dislocation and involves a kinetic process. One process that is consistent with the observed strain rate dependence is the diffusion of vacancies to the dislocation which can result in local disordering of the γ' about the dislocation, thus, producing a lowering of the APB restraining force to further dislocation motion. Accordingly, we are convinced that the strength drop-off in nickel-base superalloys is a consequence of this vacancy roughening of APB. In order to suppress such a process, one would have to essentially suppress diffusion, which is near impossible to accomplish by changes in γ' morphology or by processing means. Figure 2 uniquelly demonstrates that changes in γ' morphology will not affect the location of the knee. That this location is not affected by processing means is demonstrated by recent investigations involving thermomechanical treatments [4] and manipulation of solidification modes in nickel-base superalloys.[5] In addition, recent data also show that the strength drop-off temperature of the current high strength nickel-base superalloys is about as high as one can achieve through alloying means.

Accordingly, it appears that the upper limit of strength drop-off temperature has already been reached. The magnitude of yield strength below this temperature, however, can be manipulated. This can be done through alloying. It can also be accomplished through dislocation network strengthening, e.g. the creep induced

dislocation substructure strengthening shown in Fig. 2, see reference.[2] Similarly,
thermomechanical processing of a more violent nature than creep should also provide
dislocation network strengthening, and indeed it does.[4] Before leaving Fig. 2, let
us apply it to the ever popular subject of composite structures.

In these days of composite thinking, it is always interesting to contemplate
composite or directional eutectic structures of select phases, e.g. γ/γ' directional
eutectics instead of the traditional nickel-base superalloy strengthened by pre-
cipitated γ' particles. Figure 2 offers a brief preview of what one may expect from
eutectic-like structures of γ and γ' phases, since the stress coarsened γ' morpho-
logies, Fig. 1, bear resemblance to composite structures. Moreover, the dislocation
networks about the stress coarsened γ' rods and plates, Fig. 3, which were actually
induced by creep, can be imagined instead to be a consequence of thermal stresses,
which can and do develop between phases during eutectic solidification. Accordingly,
we conclude that below 1400°F composites of γ and γ' phases may certainly be stronger
than traditional nickel-base superalloys with similar chemistries. However, the
advantage of high temperature strengthening by composite structures may not be
intrinsic to γ/γ' systems, since independent of morphologies, composite or otherwise,
for good reasons already mentioned the yield strengths of the γ/γ' systems drop
abruptly at about the same temperature, Fig. 2.

Let us now bring back grain boundaries, which have always been the weak links in
nickel-base superalloys, and, their strengthening a challenge. We are now convinced
that as long as strengthening is accomplished through precipitated phase (γ', carbides,
etc.) or elements (boron, hafnium, etc.), there will always be the problem of
degradation of the strengthening effects during elevated temperature applications
under load. This is because stress induced diffusion between grain boundaries will
always occur and cause chemical changes at the grain boundaires.[6] These chemical

changes can result in the dissolution of strengthening phases at certain grain boundaries, Fig. 4 and 5, and thus deleteriously affect subsequent strength. Accordingly, we conclude that whereas prolonged high temperature applications under load may not adversely affect the strength of coherent particle strengthened alloys when they are used as single crystals, e.g. see Fig. 2, the same applications can result in a gradual degradation of strength when the alloys are polycrystals. This of course restricts the application of polycrystalline nickel-base superalloys to temperatures where stress induced diffusion is tolerable for the purposes at hand.

It is interesting but not surprising that diffusion is the limiting factor with respect to both intragranular strength drop-off temperature and intergranular phase instabilities. Accordingly, improvements in mechanical properties will result if, in addition to γ', phases that are immune to diffusive fluxes, i.e. insoluble phases, are also incorporated into the systems. This approach has indeed been taken by Benjamin in his work on mechanical alloying of nickel-base superalloys with inert dispersoids.[7]

On Creep

As we have discussed, above 1400°F the deformation of nickel-base superalloys becomes strain rate sensitive, i.e. thermally-assisted deformation processes or creep processes come into play. In crystalline solids creep deformation can occur by three fairly independent processes; these are grain boundary sliding, diffusional or Nabarro-Herring creep and dislocation or intragranular creep. Since the first two processes will occur only if there are grain boundaries [8-11], a major step towards achieving heaven in creep resistance is the elimination of grain boundaries. A few years ago VerSnyder, Shank, and Laboratory took this step [12], and thus began the technology of directional solidification and engineering single crystals, which continues today not only with respect to nickel-base superalloys but also in terms of other high temperature systems. With boundary-free structures in the offering, let us go on to define limits of creep of single crystals.

It is fairly well accepted that intragranular creep involves the thermally-assisted motion of dislocations [13], in particular, the motion of screw dislocations. More detailed understanding has it that the motions of screw dislocations are in turn rate controlled by the motions of jogs, which are edge segments of atomic heights on the screw dislocations.[14,15] The rate controlling process for the motion of these jogs has been proposed to be that of vacancy diffusion, i.e. the activation energy for creep is also that for self diffusion.

The steady-state creep of pure metals and solid solutions appear to be rate controlled by self diffusion. However, creep of such particle strengthened systems as TD-nickel and nickel-base superalloys are not always rate controlled by self diffusion, since high activation energies, on the order of 150-250 kcal mole^{-1}, are commonly associated with the creep of these systems. These values of activation energy are about three times that of self diffusion in nickel.

Recently, a model was proposed to explain the creep behavior of nickel-base superalloys and other particle strengthened systems.[16] In nickel-base superalloys, in order to accommodate the difference in slip occurring between γ and γ', dislocation networks start to make their appearance in primary creep and attain full development with the onset of steady state creep, where the network size becomes comparable with the γ' interparticle spacing, e.g. Fig. 3. These and other considerations led to the conclusion that the high creep activation energy in particle strengthened systems is associated with the presence of very finely meshed dislocation networks, which are naturally absent or coarser in mesh during the creep of pure metals and solid solutions. More specifically [16], mechanism for creep, hence the activation energy, depends on the scale of the dislocation networks, which are sources for jogs on mobile screw dislocations during creep. When the dislocation networks are coarse in mesh, as in single phase systems, or even in nickel-base superalloys during primary creep, the density of jogs will be small and the motion of jogs, and hence, creep, will be rate controlled by vacancy (self) diffusion, and the creep rate will be high. However, when the dislocation networks become fine in mesh, as is the case for the steady state creep of particle strengthened systems, the density of jogs will be high and local equilibrium of vacancy concentration may not be maintained at the jogs. Consequently the model proposes that the motion of jogs, and thus creep, will be rate controlled by higher activation energy processes involving interstitialcys (solute or solvent atoms in interstitial sites).[16] Thus, for a given applied load, creep rates will be slower in systems with finely meshed dislocation networks.

The above model provides us with an upper limit in the activation energy for creep, which is that for diffusion involving the formation and motion of interstitialcys. Furthermore, it appears that not much can be done to impart substantial improvements on creep of nickel-base superalloys through processing, since the steady state creep rates of superalloys are already associated with the high activation energies. The above model suggests , however, that it may be possible to eliminate the plastic strains

associated with primary creep through stress annealing prior to usage, after the manner that developed the mature dislocation network in Fig. 3. Thermomechanical processes may also eliminate or suppress primary creep.

On Fatigue

In gas turbine applications, the useful lives of nickel-base superalloys are often limited by fatigue considerations. The major reason for this limitation rests with the rather poor fatigue properties of nickel-base superalloys. This fact is perhaps most vividly displayed when one compares the ratio between endurance limit and yield strength, i.e. the normalized endurance limit of nickel-base superalloys, with those of other metals and alloys.[17] For example, the normalized endurance limit (at 10^6-10^7 cycles) of such pure metals as aluminum, copper, iron, and, nickel is about one, and those of aluminum-base alloys and iron-base alloys are about one-half to one. In contrast, the endurance limits of nickel-base superalloys are only about a quarter of their yield strengths. Indeed, nickel-base superalloys are adequate for fatigue applications only because this rather low normalized endurance limit is maintained to elevated temperatures as a consequence of the unique temperature dependence (or independence) of the yield strengths, which are also high in magnitudes.

The poor showing of nickel-base superalloys under fatigue loading conditions is fairly well understood, e.g. see reference 17. It turns out that these alloys as a consequence of their heterogeneous or planar slip mode, a behavior which as normally extends to about 1400°F, react in a fairly brittle manner to such structural heterogeneities as casting pores and crack-like, or sometimes cracked, carbide phases. Accordingly, these heterogeneities are initiation sites for fatigue fracture. The planar slip nature of nickel-base superalloys also result in crystallographic fracture, with fatigue life being determined by relatively fast crack propagation rates along the planar slip bands. We take these microstructural understandings as the guidelines

for improvements. In other words, in nickel-base superalloys the requirements for reaching the ultimate in fatigue properties rest with 1) the elimination of structural heterogeneities, and 2) the dispersion of slip. Although we are not yet in a position to peek at the effects of both 1) and 2) together on the fatigue of nickel-base superalloys, we do know the effects of their individual contributions. Let us first discuss structural heterogeneities.

An interesting feature of the plane front solidified structures is the reduction of size and density of gaseous porosity.[3,5] We associate this elimination of pores with the absence of the dendritic forest during the solidification of homogeneous cast structures, results which strongly indicate that casting porosity originates mainly from the entrapment of evolved gas bubbles by the dendritic forest during solidification. Carbides, of course, can be eliminated by purposely lowering the carbon content. The fatigue properties of carbide-free, homogeneously cast nickel-base superalloy (of MAR-M200 composition) was obtained, and as anticipated, found to be superior to those of dendritic materials.[5] For example, the normalized endurance limit (at 10^6 cycles) was found to be about 0.5 at room temperature and about 0.75 at 1200°F. These ratios are, of course, improvements over the usual 0.2 or 0.3 associated with other nickel-base superalloys, which were not plane front solidified.

In the above discussion, we have essentially shown that control of solidification or casting can lead directly to improvements of fatigue properties through producing homogeneous microstructures. Apparently, thermomechanical processes can also result in similar improvements.[4] This is consistent with the refinement (breaking-up) of brittle phases and the closing of pores and voids by mechanical working. Proceeding now to the effects of the dispersion of slip on fatigue properties, we draw upon a recent investigation dealing with the fatigue of a nickel-base alloy that exhibits many of the features of a traditional nickel-base superalloy turned inside out.[18]

Basically, the novel alloy consists of γ' [Ni_3(Al,Ta)] matrix strengthened by coherent particles of γ (nickel solid solution), Fig. 6. The intrinsic fatigue resistance of this γ' matrix alloy should prove superior to that of the traditional one, since massive γ' exhibits dispersed or homogeneous slip. The fatigue results bear this out, since the data shows that the normalized endurance limit of the alloy is at least 0.5 at room temperature.[18] In addition, fracture surface appearance suggest that the specific endurance limit of the γ' matrix alloy should be even higher, since the size and density of pores in the specimens tested are even larger than those normally found in the traditional superalloys. These pores can of course be refined, or, even eliminated by either plane front solidification or thermomechanical processes. Although elevated temperature data are not yet available, it is reasonable to presume that the endurance limit of γ' matrix superalloys, through cyclic strain hardening, should increase with increasing temperature in a manner that follows the well established temperature dependence of strain hardening of γ'.

Based on the above discussion, it appears that nickel-base superalloys have yet to fulfill their fullest potential with respect to fatigue resistance. We should all aim for an upper limit of normalized endurance limit of about unity. Processing involving either casting control or thermomechanical treatments can provide reasonable improvements in the fatigue resistance of the current nickel-base superalloys. The ultimate nickel-base alloy in fatigue resistance, however, may be that with a γ' matrix instead of a γ matrix.

Concluding Remark

The contents of this paper suggest that a near ideal nickel-base superalloy for gas turbine applications is a plane front solidified, thermomechanically treated, Gamma Prime matrix single crystal that is strengthened by Gamma particles, and, inert dispersoids. Realistic?

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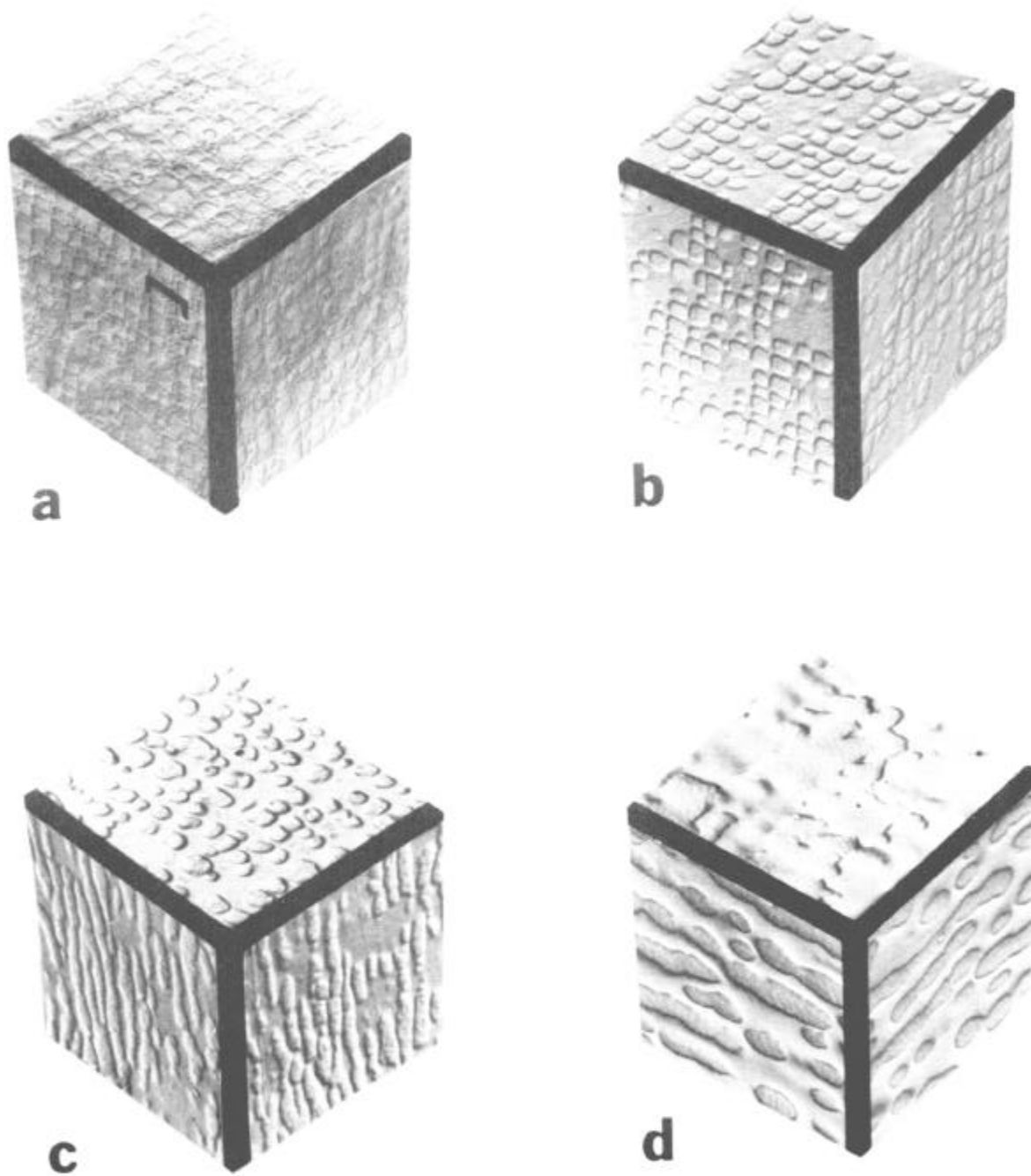18. J. K. Tien and B. H. Kear: Scripta Met., 1972, vol. 6, p. 303.

Fig. 1. <100> oriented cube representation (replica micrographs) of coherent γ'
precipitate morphology (a) after standard heat treatment, and after additional anneal-
ing for 100 hrs at 1750°F under (b) zero applied stress, (c) 22.5 ksi compressive
stress and (d) 22.5 tensile stress; stress axes were normal to top of (c) and (d)
cubes. Marker in (a) denotes 1μ.
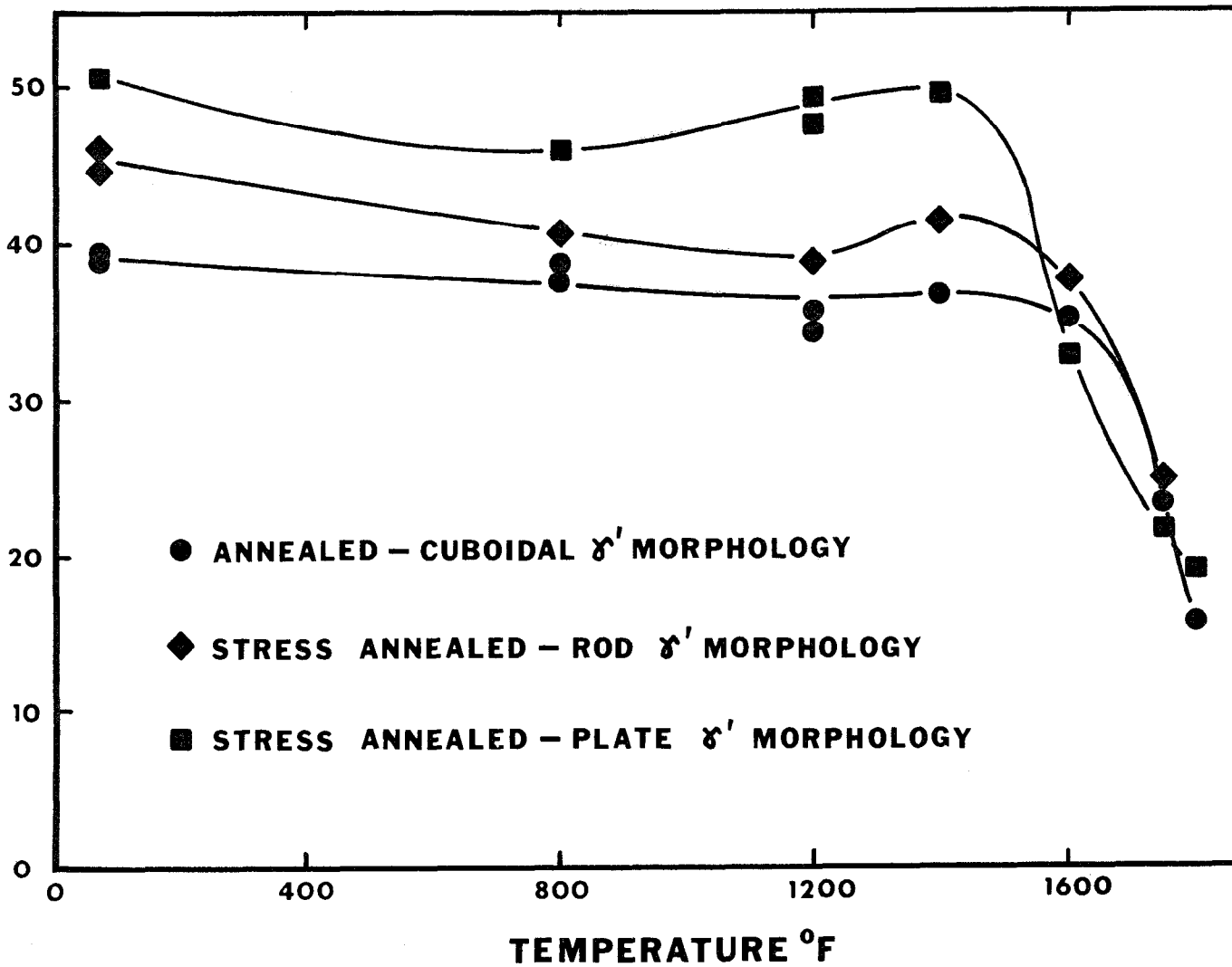
Fig. 2. Comparison of <100> yield strengths as a function of temperature for crystals with the γ' precipitate morphologies shown in Figs. 1(b), 1(c 1(d). Tensile tests axis was parallel to the γ'rods of Fig. 1(c) and normal to the γ'plates of Fig. 1(d). Data are obtained at 0.2 pct strain.

W-14
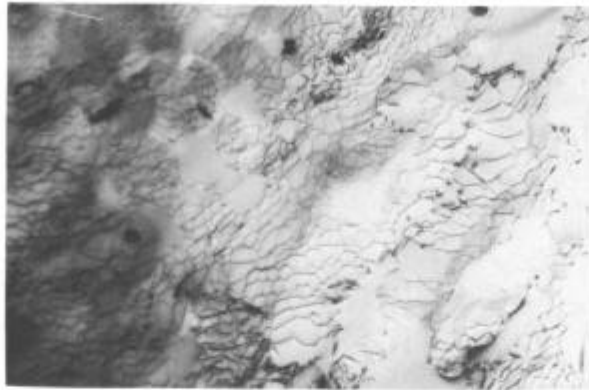
Fig. 3. Bright-field electron micrograph of 2 x 3 1/2μ region,
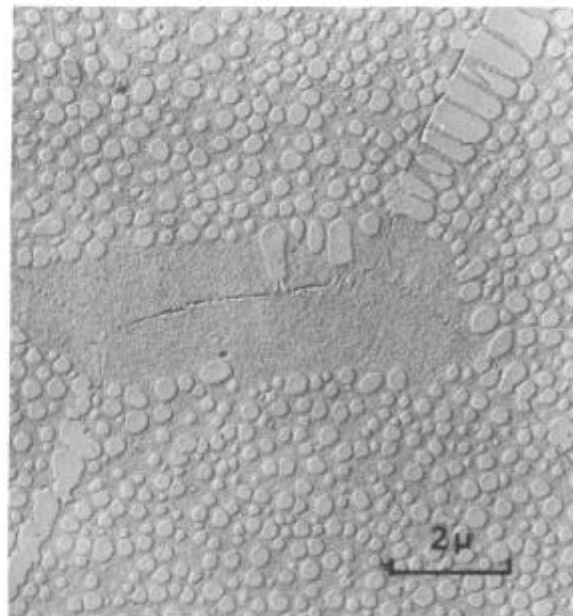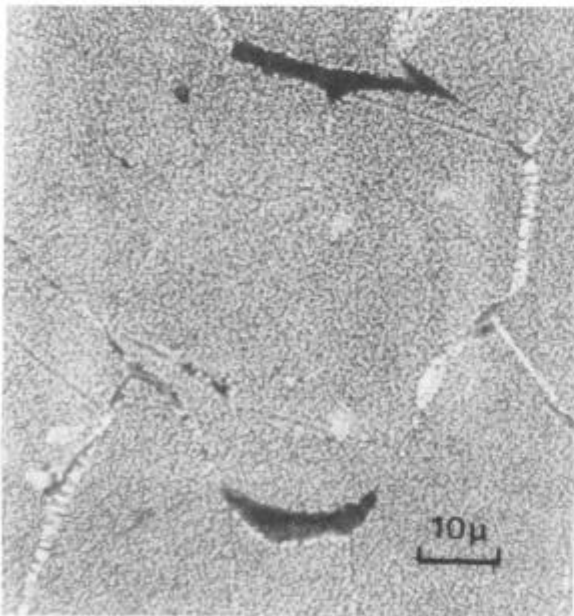showing network about γ' after annealing under
applied stress.

Fig. 4. Microstructure produced by tensile creep and resulting stress induced diffusion
between grain boundaries, showing a denudation of precipitates and increased
volume fraction of precipitates at grain boundaries transverse to and parallel to
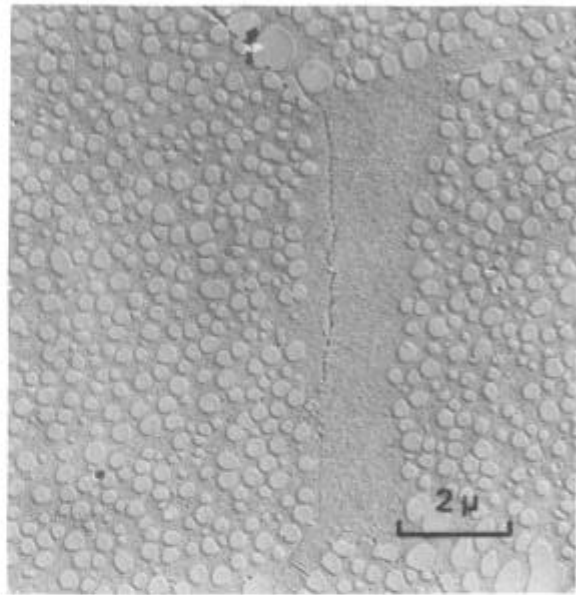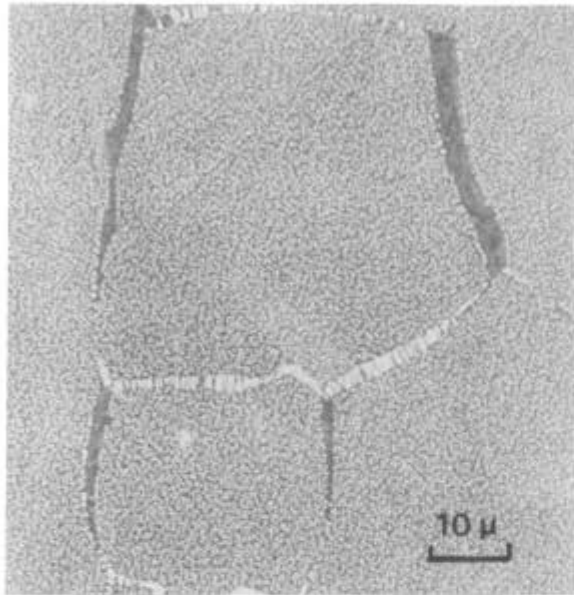the stress axis (vertical), respectively.

Fig. 5. Microstructure produced by compressive creep, showing morphology changes at
grain boundaries in the opposite sense of those due to tensile creep (Fig. 4), as
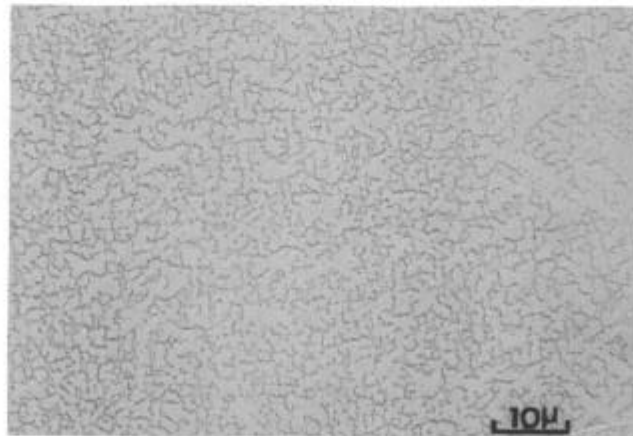consistent with the change in the sense of the stress induced solute flux.

Fig. 6. Microstructure of a nickel-base superalloy
turned inside out: lacy γ particles in γ'
matrix.