FORMATION OF TOPOLOGICALLY CLOSED PACKED PHASES IN NICKEL BASE SINGLE CRYSTAL SUPERALLOYS

R Darolia, DF Lahrman, RD Field

Engineering Materials Technology Laboratories

GE Aircraft Engines
Cincinnati, Ohio 45215
and
R Sisson
Worcester Polytechnic Institute
Worcester, MA 01609

ABSTRACT

The formation of topologically closed packed (TCP) phase was studied for a series of nickel base superalloys containing rhenium. The alloys were found to form three types of TCP phases: rhombohedral mu, tetragonal sigma and a relatively unknown orthorhomic phase, P. The crystal structures of these phases are closely related. They often coexist in the alloy, even within the same precipitate. The segmented appearance of the precipitates is due to a "basket weave" morphology, consisting of ribbons of precipitates, overlapping at 90 degree angles. Computer programs such as PHACOMP which are used to predict alloy stability do not necessarily provide good correlation with TCP formation in Re containing alloys. The paper describes in detail the nature and formation of TCP phases in one specific alloy composition.

Superalloys 1988
Edited by S. Reichman, D.N. Duhl,
G. Maurer, S. Antolovich and C. Lund
The Metallurgical Society, 1988

INTRODUCTION

The development of advanced turbine nickel base superalloys has progressively produced more complex alloy compositions in the quest for higher strengths and operating temperatures. With this increase in complexity comes an increase in the difficulty of predicting and controlling the formation of topologically close packed (TCP) phases. These phases have long been associated with property reduction as sites for crack initiation, or simply by robbing the matrix of solid solution strengthening alloying elements. In many instances, in alloys prone to TCP phase formation, short time properties (tensile properties) are not affected, but the long time creep rupture properties are severely degraded. Understanding the formation of these phases is particularly important, since the alloy developer is generally working on the edge of phase instability, in order to achieve the best balance of properties.

Today's superalloys contain high levels of refractory elements, such as Mo, W, Re, and Ta, in order to increase high temperature creep and rupture properties. These elements act as solid solution strengtheners in both the gamma and gamma prime phases. Re is a particularly potent strengthener, residing mainly in the gamma phase and is thought to retard gamma prime coarsening. High levels of these alloying elements can make the alloys prone to TCP phase formation. The control of TCP phases by judicious selection of strengthening elements is required. This has prompted the current investigation, in which TCP phase formation has been studied for a series of alloys containing Re. The nature of the phases, their relationship with the matrix and with each other, as well as the role of Re, has been investigated.

EXPERIMENTAL PROCEDURE

Several single crystal superalloy compositions were evaluated by GE Aircraft Engines in a study of the formation of TCP phases as a function of composition and exposure conditions. This paper describes results of such an investigation on a superalloy designated "Alloy 800", the composition of which is listed below in wt%:

Ni	Cr	Co	Mo	W	Ta	Ti	Al	Re
63.6	8.0	7.5	1.5	4.0	5.0	1.5	5.8	3.0

The fully solutioned and aged specimens were exposed at 1600, 1800, 2000, 2100 and 2200°F for times up to 1000 hours to determine theoccurrence of TCP phases. The TCP phases were identified using a variety of analytical electron microscopy (AEM) techniques. Crystallographic analysis was conducted using both selected area diffraction (SAD) and convergent beam electron diffraction (CBED) techniques. Energy dispersive spectroscopy (EDS) of characteristic X-rays was used for compositional analysis. In addition, scanning electron microscopy (SEM) was used to evaluate the morphology and distribution of the extracted precipitates.

RESULTS

Table I lists the temperature and time combinations which led to precipitation of the TCP phases. A time temperature transformation (TTT) curve, constructed from the data presented in Table 3, is given in Figure 1.

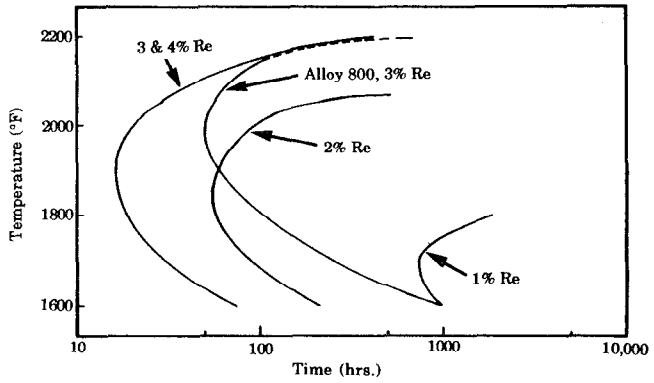


Figure 1. Comparison of TTT curve for formation of TCP phases in Alloy 800 with those of alloys 240 through 243[1].

Table I: Time for Start of TCP Phases at Various Temperatures of Exposure for Alloy 800.

Time Hours	Temperature 1600°F	1800°F	2000°F	2100°F	2200°F
20	N	N	N	N	N
35	N	N	T	N	N
50	N	N	T	N	N
75	N	N	TCP	T	N
100	N	T	TCP	T	N
500	N	TCP	TCP	-	-
1000	T	TCP	TCP	-	-

N = None, T = Trace Amounts of TCP, TCP = minor to moderate amounts of TCP.

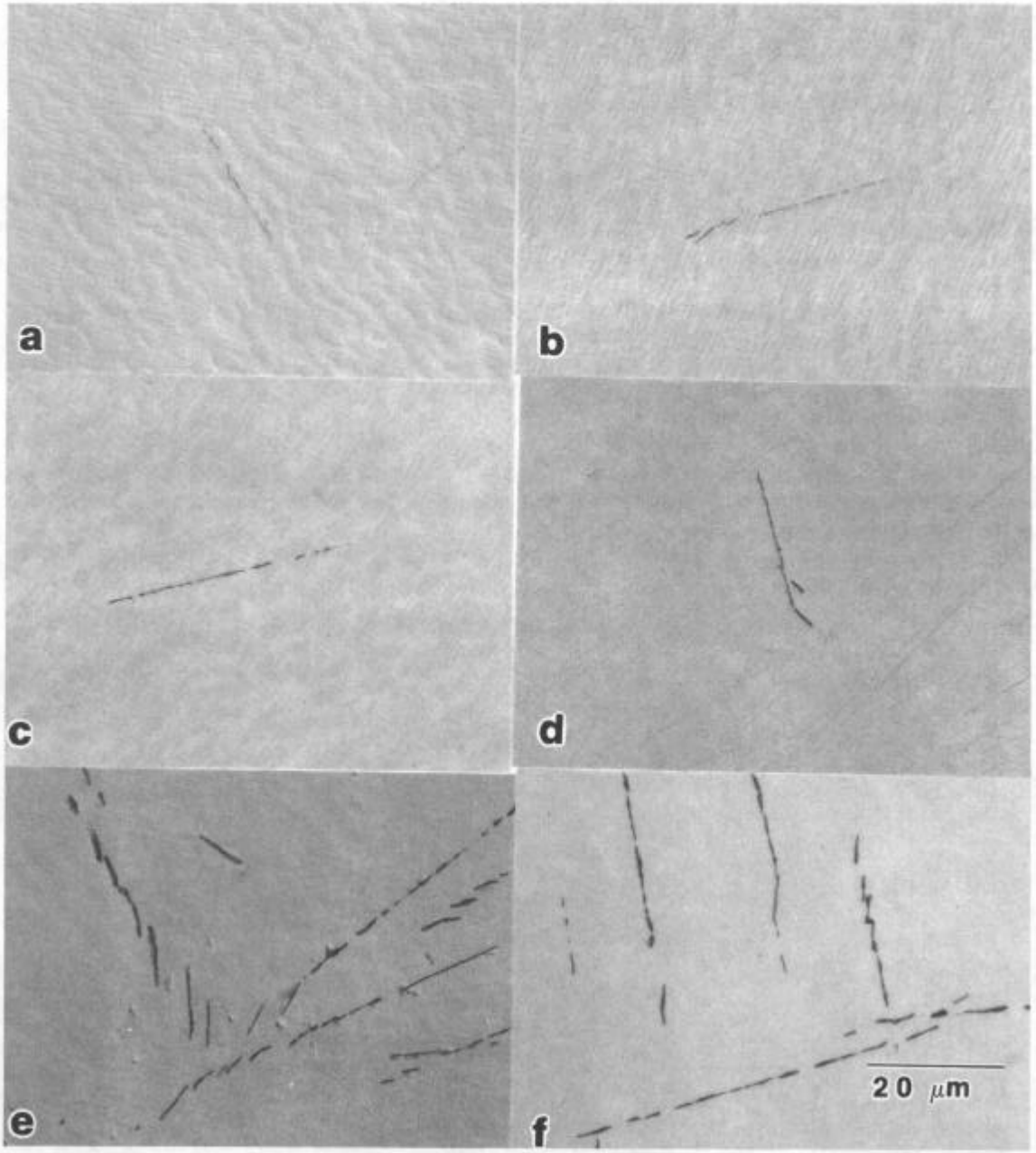


Figure 2. Optical micrographs showing the morphological development of the TCP phases at 2000°F a) 35 hrs., b) 50 hrs., c) 75 hrs., d) 100 hrs., e) 500 hrs., and f) 1000 hrs.

Also included in Figure 1 are TTT curves for other Re containing alloys (1). Figure 2 shows the morphology of the TCP phases for several exposure times at 2000°F. It is apparent that they increase in quantity and size as the time is increased. The precipitates in Figure 2 have a segmented morphology which was observed in several alloys at all stages of development of the TCP phases.

TEM observations revealed the presence of three different TCP phases in the Re containing superalloys: rhombohedral mu, tetragonal sigma, and a relatively unknown orthorhombic phase, P. The P phase was first observed by Rideout et al (2) in the Cr-Ni-Mo system. Its crystal structure was determined by Shoemaker et al (3) to be orthorhombic and is very closely related to sigma. Crystal structure information for the three phases is given in Table II.

Table II: Crystal Structure Information on Mu, Sigma, and P

TCP Phase	Space Group	Pearson Symbol	Lattice Parameter (Å)
Sigma	$P4_2/mnm$	tP30	a=9.3, c=4.86
P	Pnma	oP56	a=17.2, b=4.86, c=9.2
Mu	$R\bar{3}m$	hR13	a=9.0, a=30.8

The P and sigma phases were predominant, and appeared as platelets with {111}gamma habit planes. Electron diffraction data for sigma and P are given in Figure 3. In many cases, sigma and P were found to coexist in the same platelet. As observed in the optical and SEM micrographs, the platelets were often segmented in nature. Figure 4a shows a TEM micrograph of a sigma/P precipitate along with selected area diffraction patterns from each phase. The orientation relationships between the two phases and the gamma matrix were found to be:

$$[100]_{sigma} \parallel [100]_P \qquad [1\bar{1}0]_{sigma} \parallel [102]_P \parallel [\bar{1}12]_{gamma}$$
$$[110]_{sigma} \parallel [10\bar{2}]_P \parallel [110]_{gamma} \qquad (001)_{sigma} \parallel (010)_P \parallel (1\bar{1}1)_{gamma}$$

Thus, the habit plane for the platelets in terms of the TCP phase crystal structure is $(001)_{sigma}$ and $(010)_P$. The relationship between the sigma and P phases is depicted graphically in Figure 4b. The P phase was found to exist in two different variants within the same platelet, with the (010) planes parallel for the two variants, and $[100]_{P1}$ parallel to $[001]_{P2}$.

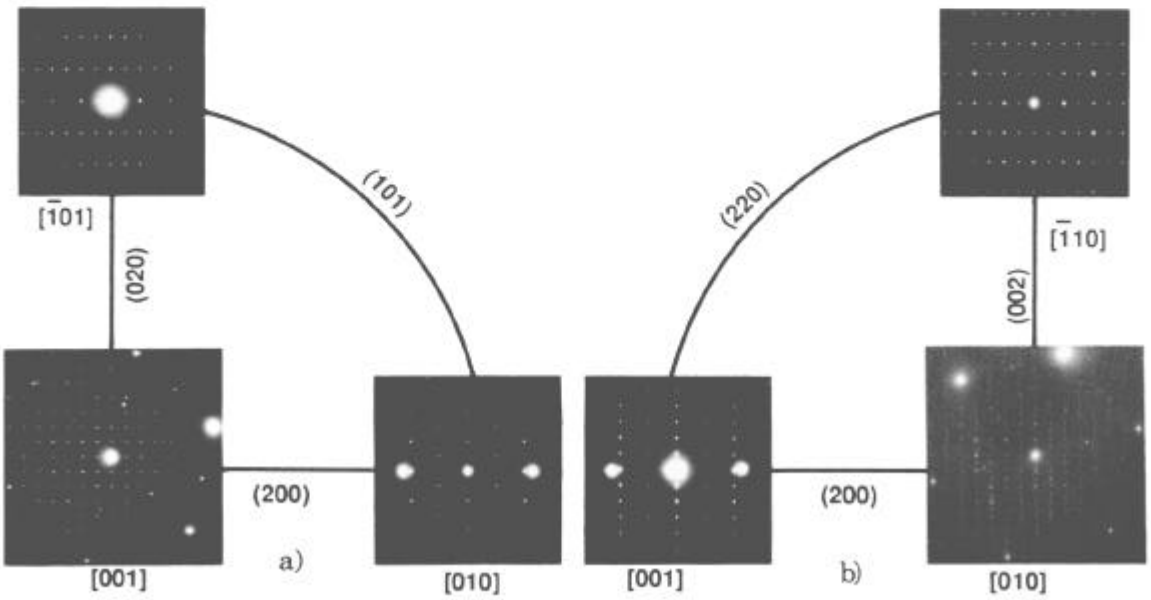
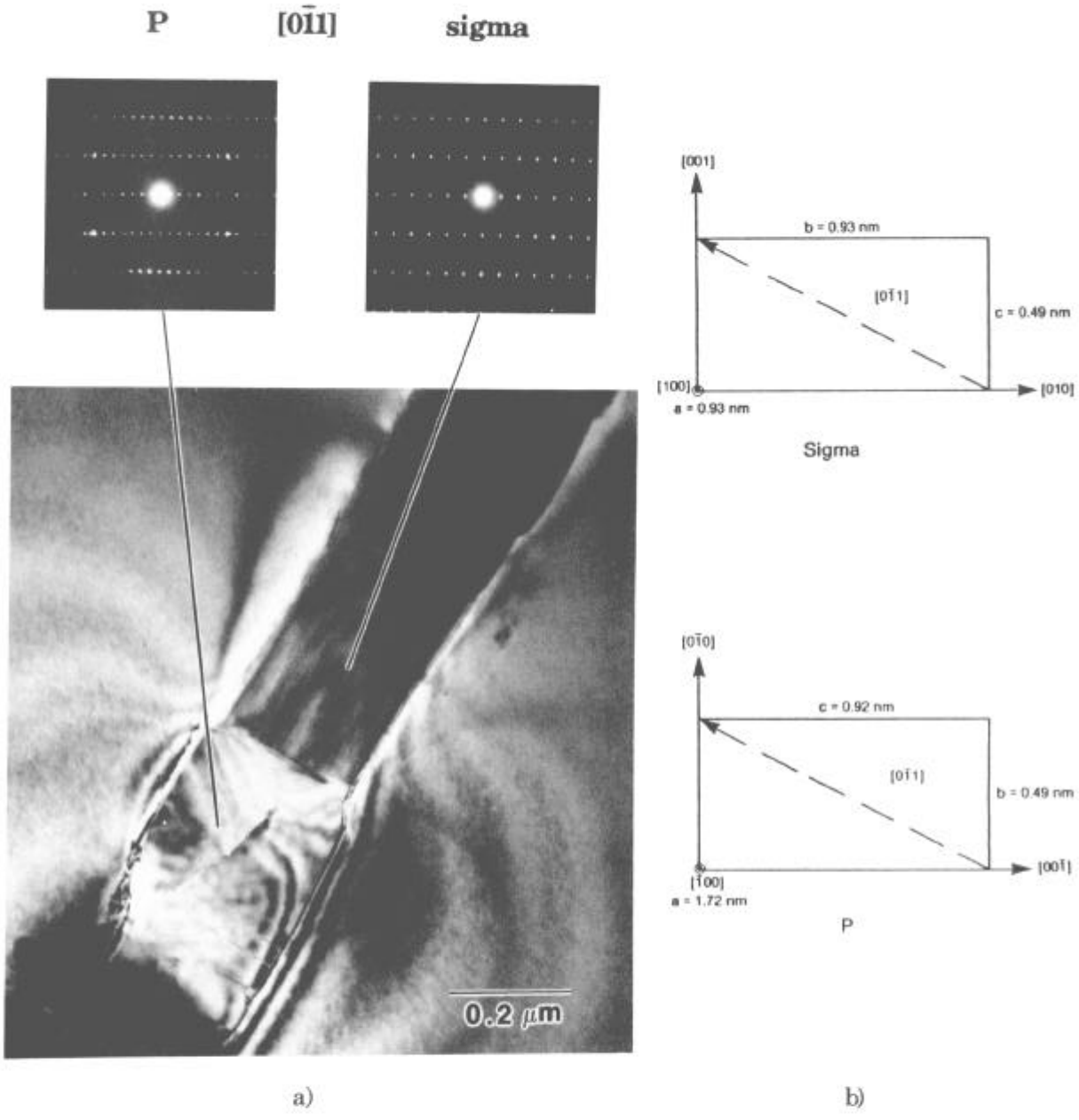


Figure 3. Selected area diffraction patterns from a) sigma precipitate, b) P precipitate in Alloy 800.



a) b)

Figure 4. a) TCP precipitate consisting of P and sigma sections.
b) relationship between the sigma and P crystal structures.

The morphology of the segmented plates is shown in Figure 5. In Figure 5a, an SEM micrograph is given of a specimen which was electropolished to show the TCP particles in three dimensions. This particle was extracted and placed on a carbon grid for TEM analysis. As shown in Figure 5b, the TCP phase has a "basket weave" morphology, consisting of ribbons of primarily P with some sigma, at 90 degree angles. The growth direction of the ribbons was found by diffraction to be <100> and [001] for sigma and P, respectively.

Figure 5a. SEM micrograph of TCP precipitate after 75 hrs. at 2000°F.

X-ray energy dispersive spectra (EDS) taken from the TCP phases in the AEM are given in Figure 6. Also included in this Figure is a spectrum taken from a sigma plate in a Ni base superalloy not containing Re. These spectra were analyzed using a peak intensity ratio technique to determine compositions of the phases. Results from these analyses are given in Table III. These compositions are semiquantitative and are included for rough comparison only. Two observations from the EDS data are of interest. Firstly, the phases have very similar compositions. The P and sigma phases are essentially indistinguishable, while the mu has somewhat higher W/Re and Co/Ni ratios, but still has quite a similar composition. Secondly, the phases in the Re containing alloy contain a high percentage of Re, far greater than what would be expected from a simple substitution of Re for other refractory elements. In fact, examination of the data indicate that Re is substituting for Cr in the TCP phase.

Table III: Results From Analysis of EDS Spectra From TCP Phases in At %

Element	P or Sigma	Mu	Sigma without Re
Ni	32	25	22
Re	19	18	-
W	8	11	5
Mo	6	7	6
Cr	25	25	54
Co	10	15	12

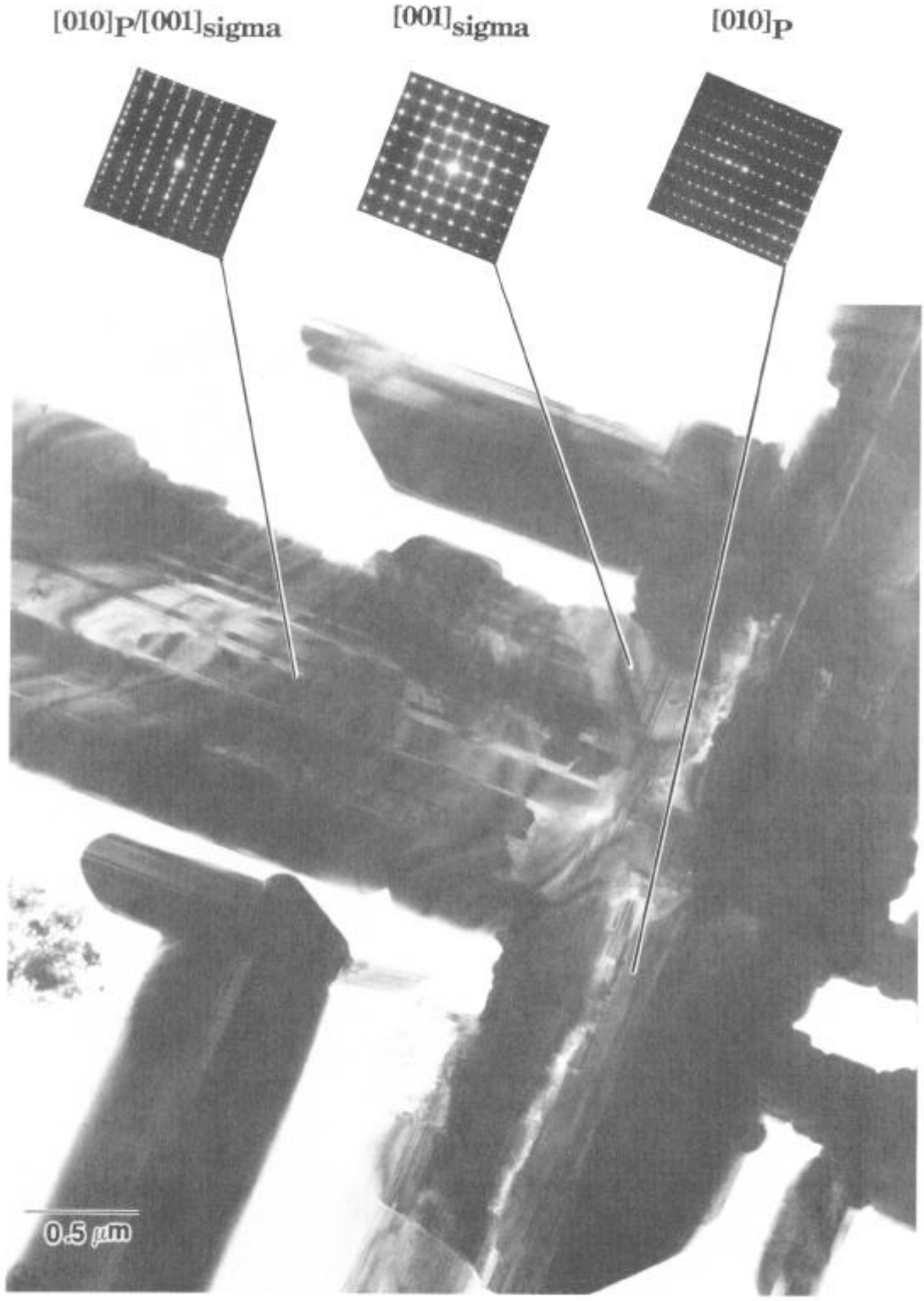


Figure 5b. TEM micrograph of extracted TCP precipitate after 75 hrs. at 2000°F. Note the crystallographic relationships between the various segments of the precipitate.

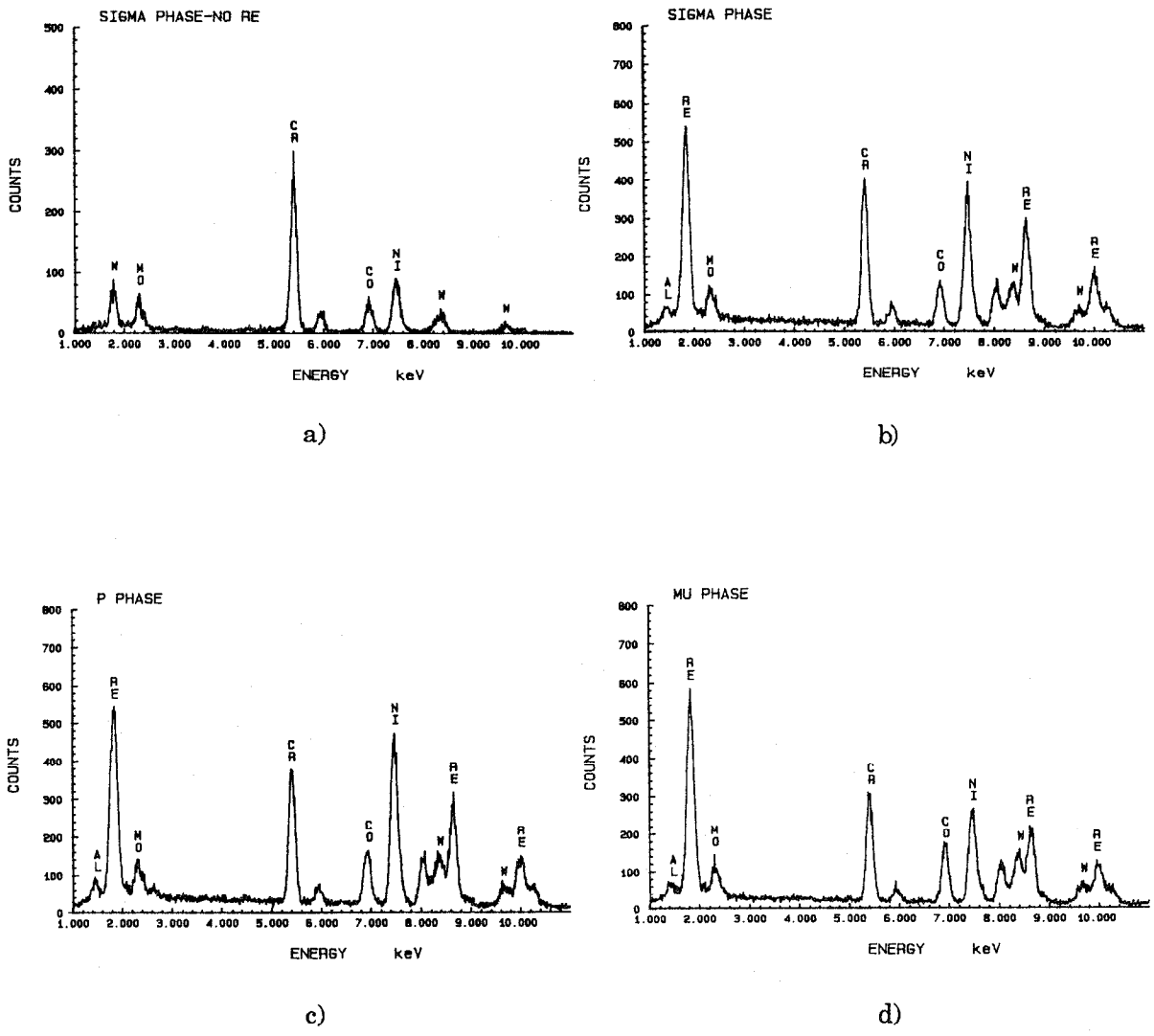


Figure 6. EDS spectra from TCP phases (a) Sigma phase in an alloy not containing Re, (b) sigma, (c) P, and (d) mu phase in an alloy containing Re.

DISCUSSION

Computer programs such as PHACOMP (N_v) are generally used to predict the overall tendency to form TCP phases. Recently, a new PHACOMP (Md) was introduced (4) for better predictive capability. It is interesting to note that the PHACOMP N_v and Md values of the alloys listed in Table IV are essentially the same, even though they behave differently with respect to TCP phase formation. This is not surprising, because the calculation of the alloy stability numbers such as N_v or Md ignores the synergistic effects of the alloying elements on their partitioning behavior. As an example, it is generally assumed that Re partitions mostly to the gamma phase. In reality, Re can partition to gamma prime. As shown in Figure 7, the addition of 2 atomic (6 weight) percent W causes up to 20% of the Re present in the alloy to partition to gamma prime (5). It is quite clear that, though the calculation of N_v and Md for phase stability is a useful guide as a first approximation, total reliance or these calculations is not recommended.

Table IV: Compositions of Alloys in Figure 1 (wt%) and Their Nv and Md Valves

Alloy	Cr	Co	Mo	W	Ta	Ti	Al	Re	Ni	Nv	Md
800	8.0	7.5	1.5	4.0	5.0	1.5	5.8	3.0	63.6	2.19	0.9244
240(1)	7.5	5.0	2.0	3.0	12.0	1.0	5.0	1.0	63.5	2.15	0.9233
241(1)	7.5	5.0	2.0	2.0	12.0	1.0	5.0	2.0	63.5	2.15	0.9211
242(1)	7.5	5.0	2.0	1.0	12.0	1.0	5.0	3.0	63.5	2.14	0.9209
243(1)	7.5	5.0	2.0	0.0	12.0	1.0	5.0	4.0	63.5	2.14	0.9197

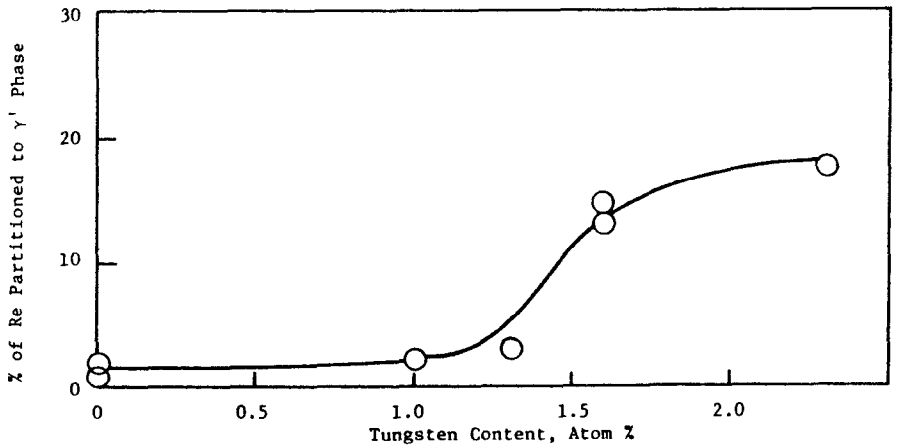


Figure 7. Plot showing synergistic effects of W and Re on gamma/gamma prime partitioning of Re.

The similarity of the compositions of the P and sigma phases, and their orientation relationship within the platelets, can be understood if one examines the crystal structures of the phases shown in Table II. Sigma is tetragonal, with a=0.93 nm and c=0.49 nm. P is orthorhombic with a=1.72 nm, b=0.49 nm, and c=0.92 nm. As can be seen from these parameters, the 'a' parameter of the P unit cell is approximately twice that of sigma and the two phases are very closely related crystallographically (3). Thus, the energy difference between the two phases is quite small, and they are found to coexist in the microstructure with almost identical compositions. Due to the difficulty in distinguishing between the two phases in the AEM, the precise conditions under which P or sigma preferentially precipitate were not determined.

It is interesting to consider the origin of the segmented plate morphology observed in the optical micrographs. One possible explanation for the morphology is the existence of a "precursor" phase, which is continuous. The original continuous phase may become segmented or serve as a nucleation site for other precipitates, thereby maintaining a common growth plane. However, examination of specimens aged for short times revealed the presence of segmented plates even at the earliest stages of precipitation. The other possibility is that the segments are actually connected in three dimensions, and that the segmented appearance represents a growth morphology within the habit plane. This may be due to slow growth of the TCP phase in the gamma prime phase in which the concentration of TCP forming elements is low, yielding a "swiss cheese" morphology of a plate with holes, or some other growth morphology inherent in the TCP structure itself.

As observed in Figure 5, the segmented plates seen in three dimensions display a "basket weave" morphology, consisting of ribbons of precipitate, overlapping at 90 degree angles. Although these precipitates maintain the {111}gamma habit plane determined by their orientation relationship with the matrix, the "basket weave" morphology is determined by the crystallography of the TCP phases themselves. Thus, the 90 degree angles between the ribbons is a manifestation of the [001] growth direction for P or <100> growth direction for sigma. It

should be noted that these directions are essentially equivalent, parallel to the 0.92nm lattice parameter of the two unit cells. The fact that only one such direction exists in the P structure, the predominate phase, probably gives rise to the ribbon morphology. The precipitates appear to have grown as "solid state dendrites" within the {111}gamma habit plane. This is thought to be caused by the preferred growth direction of the platelets combined with the diffusion fields of the TCP forming elements within the matrix. Thus, a perturbation along the side of a ribbon of TCP phase would extend into a region with a higher concentration of TCP forming elements (ie. outside the depleted zone surrounding the precipitate) and become stable, in a solid state analogy to dendritic growth at a liquid/solid interface. The slow diffusion rates of the TCP forming elements, particularly Re which is a major constituent of the precipitates in these alloys, promotes this growth mechanism. In the case of P phase precipitates, the growth of one of these "secondary arms" involves the formation of a low energy interface to create a variant with the [001] growth direction at 90 degrees to that of the original precipitate. The precipitates are heavily faulted, and the formation of such an interface would not be difficult. The 4-fold symmetry of the sigma (001) axis precludes the necessity of such a variant.

SUMMARY

From the data presented here, it is clear that Re plays a special role in the formation of TCP phases in Ni base superalloys. It is a potent TCP former which does not act similarly to other refractory elements, such as W and Mo, but appears to substitute for Cr in the TCP phase. Computer programs such as PHACOMP which are used to predict alloy stability do not necessarily provide good correlation with TCP formation in these Re containing alloys and it seems that the way in which Re is treated in such programs requires reevaluation.

It is evident that Re containing alloys can be unstable with respect to three types of TCP phases: mu, sigma, and P. These phases often coexist in the alloy, even within the same precipitate, with very similar compositions. The crystal structures of these phases are closely related, particularly sigma and P, and it is likely that such multiple phase TCP precipitates exist in non-Re containing alloys as well. Thus, "sigma" formation , in these alloys at least, is more complicated than is traditionally believed.

Lastly, the origin of segmented plates of TCP phase involves a growth mechanism inherent in the phases themselves. Upon examination in three dimensions, it is found that they grow on the {111}gamma habit planes as "solid state dendrites" with preferred growth directions defined by the crystallography of the TCP phases. This also may be promoted by diffusion gradients around the growing precipitates. The relative detrimental effects of "segmented" versus continuous plates is not known.

ACKNOWLEDGMENTS

The authors wish to sincerely acknowledge the contributions of the following people: Dr. Stanley T. Wlodek for SEM analysis of the TCP phases, Mr. James C. Nickley and Mr. John Snyder for their work at various stages of the investigation.

REFERENCES

1. S. Chin and D.N. Duhl, "Evaluation of Advanced Single Crystal Superalloy Compositions", Final Report NADC 78120-60, (1980).

2. S. Rideout, W.D. Manly, E.L. Karmen, B.S. Lament and P.A. Beck, J. Metals/Trans AIME, Oct. (1951), 872-876.

3. D.P. Shoemaker, C.B. Shoemaker and F.C. Wilson, Acta Cryst., 10 (1957), 1-14.

4. M. Moringa, N.Yukawa, M. Adachi and H. Ezaki, "New PHACOMP and its Applications for Alloy Design", Superalloys 1984 Eds. M. Gell, et. al., (American Society of Metals, Metals Park, Ohio 1984), 523-532.

5. M.L. Frey and P. Aldred, "Effect of Rhenium on the Properties of Superalloys", General Electric Report No. R75AEG189, (1975).