EFFECT OF MINOR ELEMENTS

ON THE DEFORMATION BEHAVIOR OF NICKEL-BASE SUPERALLOYS

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Abstract

Alloying with the minor elements carbon, boron, zirconium, and hafnium has played a very critical role in the development and application of nickel-base superalloys. The elements are known to improve strength and grain boundary cohesion, but a clear understanding of the underlying mechanisms has been lacking. To systematically address this, a series of 15 polycrystalline alloys were prepared with various minor element additions using Alloy 454 (alloy chemistry of PWA 1480) as the base alloy. Intermediate temperature (1400°F) creep testing was used as a means for evaluating the effectiveness of the minor elements. Typically, a fifty-fold improvement in creep-rupture life was attained with ~0.5 atom percent minor element additions. Although the increase in elongation to failure, in an engineering sense, was insignificant, the synergistic effect of adding combinations of the elements resulted in even greater enhancements. It was not possible to rationalize the results with any consistent grain boundary microstructural changes. To further understand the effects of minor element additions, eight single crystal alloys were cast with optimum additions of minor elements using Mar-M200 as the base alloy. Intermediate temperature (1400°F) creep behavior was evaluated in the three major orientations <001>, <011>, and <111>. In general, the addition of the minor elements did not alter the behavior of the <001> or the <011> orientations, but decreased the creep resistance of the <111> orientation. Again, the synergistic effect of combinations of the minor elements was very significant. The decrease in the creep rate of the polycrystalline material is believed to be a manifestation of the mechanism that leads to the decrease in the creep rate of <111> oriented single crystals. This in turn is attributed to an intrinsic strengthening of the cube slip system which is geometrically favored near the <111> orientation. It is proposed that the suppression of cube slip, with lower multiplicity than octahedral slip, enhances strain compatibility in the grain boundary regions. These areas are enriched in the minor elements, due to preferential segregation of minor elements to the grain boundaries.

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Introduction

Alloying with the minor elements carbon, boron, zirconium, and hafnium has played a very critical role in the development and application of nickel-base superalloys (1). Ductile polycrystalline superalloys would not be a practical reality without the presence of these elements within a narrow composition range well defined by experience. Similarly, hafnium additions to directionally solidified superalloys has been found to be a significant milestone in the application of columnar grained hollow turbine airfoil castings (2). While the underlying mechanisms are not well understood, the benefits of adding minor elements to nickel-base superalloys are generally believed to be related to improvements in grain boundary strength and cohesion. With the advent of single crystal nickel-base superalloys, these elements were deemed unnecessary and their concentration reduced to increase alloy melting point, widen the solution heat treatment range, and broaden alloying flexibility (3). While interest in minor element additions to superalloys has matured, the ductilizing effect of boron additions to the intermetallic compound Ni_3Al is generating renewed enthusiasm for the application of the concept to other high temperature materials and in particular intermetallics (4).

Preferential segregation of minor elements to grain boundaries is easily rationalized on the basis of the atomic size difference of over 25 percent between the minor elements and the average size of the nickel atom. Consequently, it is natural to attribute and limit the role of minor elements to grain boundaries and a host of mechanisms related to second phases, microstructural changes, electronic structure, scavenging effects, and other processing effects (5,6). To systematically understand the effect of minor elements, an intermediate temperature creep study of a series of minor element modified polycrystalline superalloys was undertaken. The experimental details and results of this study are presented in Part I below.

Besides these obviously grain boundary related mechanisms, the intrinsic effect of these elements on the deformation behavior of the grain cannot be ignored. A comparison of the yield strength anisotropy of single crystal Mar-M200 with minor elements (7) and PWA 1480 with no minor elements (8) first hinted at such a possibility. To establish the validity of any intrinsic effect of the minor elements, the effect of these elements on single crystal superalloys was also evaluated. The experimental details and results of this effort are presented in Part II of this paper. This is followed by a discussion of a consistent reconciliation of the results of both Parts I and II in terms of the intrinsic effects of minor elements on the slip behavior of superalloys.

Part I - Polycrystalline Alloys

Experimental Procedure

A series of 15 polycrystalline alloys were prepared with varying concentrations of carbon, boron, zirconium, and hafnium individually, with four of these alloys having combinations of these elements as presented in Table I. Alloy 454 (alloy chemistry of PWA 1480) was chosen as the base alloy, and minor elements were added as late additions using a conventional casting process. The liquidus and solidus temperatures were determined using differential thermal analysis (DTA) as listed in Table I, and subsequently casting parameters were adjusted to avoid unusually coarse grain material. All the cast material was hot isostatically pressed (HIP) and heat treated at temperatures listed in Table I. Intermediate temperature creep testing (1400°F/45 ksi) was used as a sensitive means for evaluating the effectiveness of the minor elements.

Table I. Composition, DTA Results and Heat Treatment Temperatures of Conventionally Cast Polycrystalline Alloys

Alloy	Weight % Minor Elements C	B	Zr	Hf	DTA Results Liquidis °F	Solidus °F	HIP Temp. °F	Solution Heat Treat Temp. °F
454	-	-	-	-	2485	2377	2250	2350
455	0.018	-	-	-	2477	2372	2250	2350
456	0.062	-	-	-	2477	2346	2250	2350
457	0.12	-	-	-	2477	2379	2250	2350
458	0.15	-	-	-	2483	2379	2250	2350
459	-	-	-	0.38	2467	2307	2150	2225
460	-	-	-	1.05	2468	2205	2150	2175
461	-	0.015	-	-	2464	2288	2150	2225
462	-	0.10	-	-	2451	2249	2150	2175
463	-	-	0.05	-	2477	2366	2250	2325
464	-	-	0.1	-	2464	2359	2250	2325
465	-	0.015	0.05	-	2470	2359	2250	2275
466	0.1	0.015	0.05	-	2468	2373	2250	2275
467	0.1	0.015	0.05	1.0	2462	2225	2150	2175
468	0.05	0.1	0.05	-	2462	2221	2150	2175

Base Composition: Ni-5 Co-10 Cr-4 W-12 Ta-5 Al-1.5 Ti (weight %)
Heat Treatment: HIP 4 hours/15 ksi + Sol. heat treat. 4 hours/air cool + 1975°F/4 hours + 1600°F/32 hours

Results

The creep curves for alloys with individual additions of carbon, boron, zirconium, or hafnium along with a creep curve for the minor element free baseline Alloy 454 are presented in Figures 1(a) through 1(d), respectively. Results for alloys with combinations of the minor elements are presented in Figure 2. It is clear from Figure 1 that among the individual elements, zirconium is the least and hafnium the most effective in reducing the creep rate. The synergistic effect of combining the elements was very great as evident in Figure 2. In all cases, improvement in rupture life is a result of a significant decrease in the minimum creep rate. The increase in the elongation to failure from 0.1% to 0.5%, in an engineering sense, is not very significant. These results could not be rationalized with any consistent microstructural changes. For example, a fivefold decrease in the grain size between hafnium modified alloys and alloys modified with a combination of minor elements does not have any significant effect on creep behavior. In all cases, except carbon, the rupture life continually improves with increasing concentrations of the minor elements. In the case of individual additions of carbon, 0.05 weight percent seems to be optimum. Typically, a fifty-fold improvement is attained with ~0.5 atom percent additions as shown in Figure 3, where the rupture life is plotted against total analyzed atom percent of the minor elements. Beyond that concentration level, the gain is marginal or declines for the case of carbon.

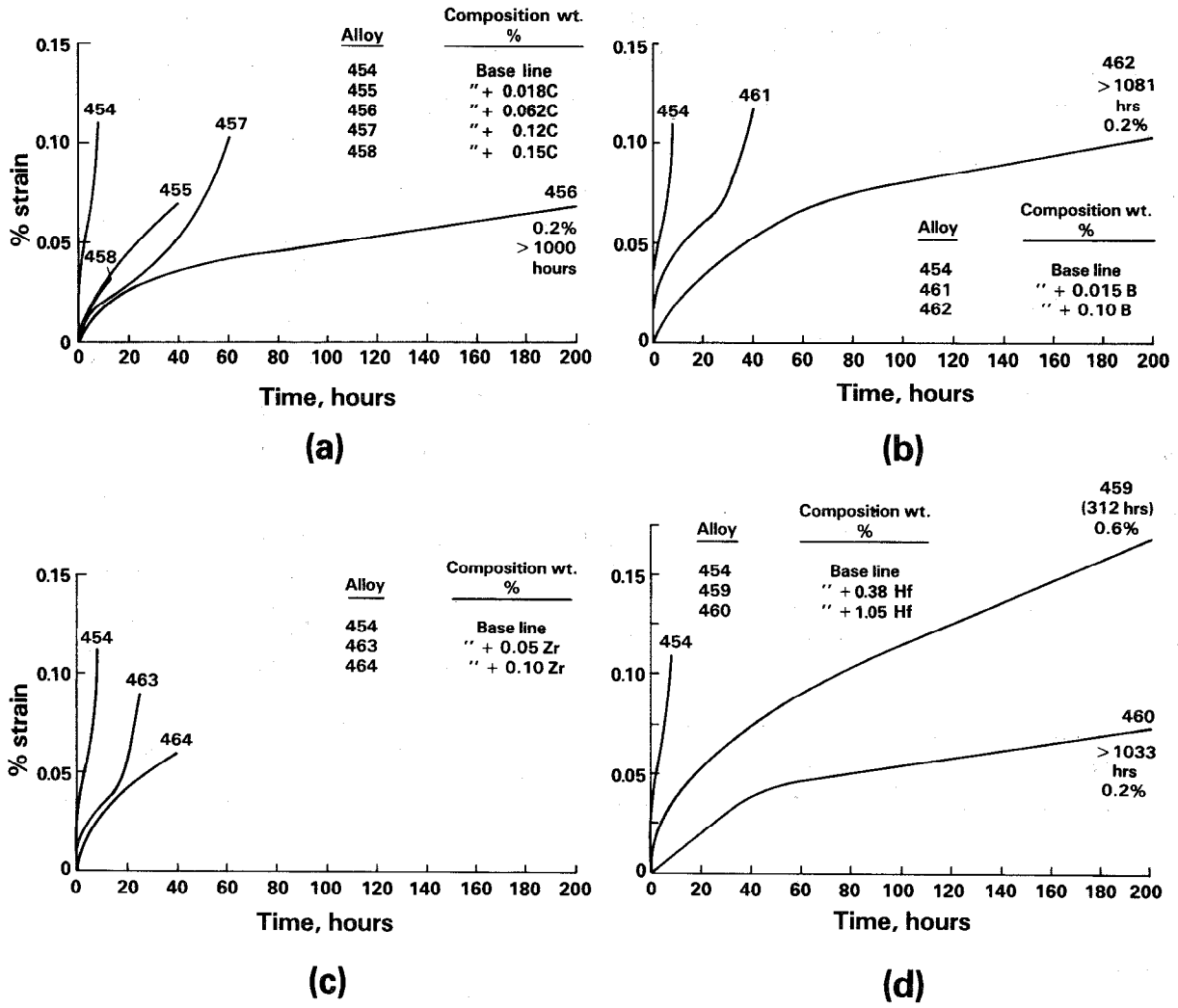

Figure 1 - Effect of individual additions of minor elements (a) carbon, (b) boron, (c) zirconium, and (d) hafnium, on 1400°F/45 ksi tensile creep behavior of conventionally cast polycrystalline alloys.

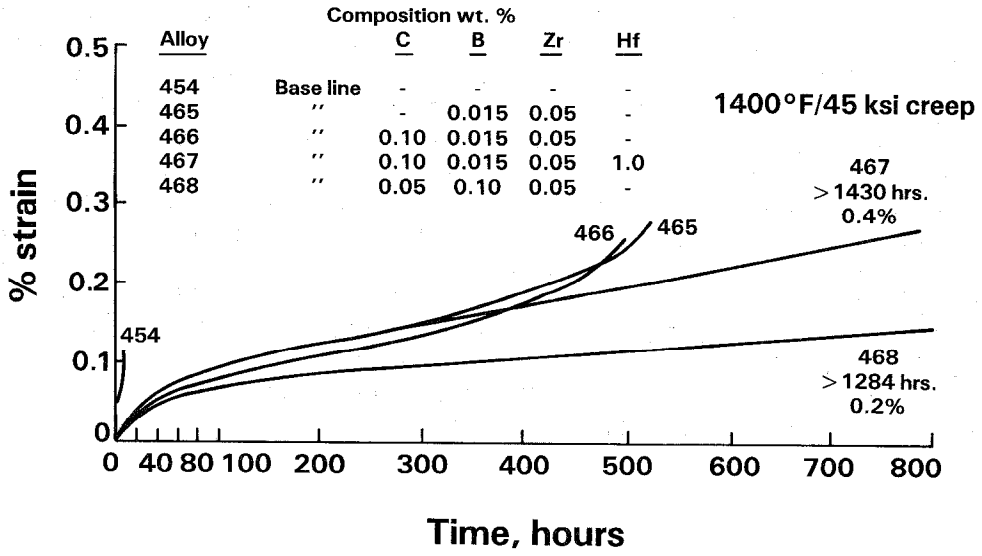

Figure 2 - Effect of combined additions of minor elements on 1400°F/45 ksi creep behavior of conventionally cast polycrystalline alloys.

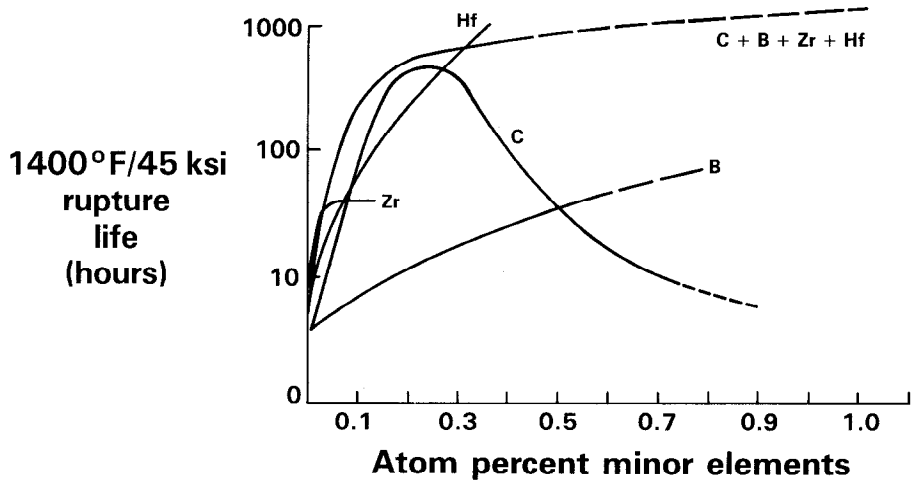

Figure 3 - Rupture life at 1400°F/45 ksi versus total atom percent of minor elements in conventionally cast polycrystalline Alloy 454.

Part II - Single Crystal Alloys

Experimental Procedure

In the second part of this study, single crystals of a series of eight alloys were cast using a Mar-M200 baseline. These included one alloy devoid of minor elements; four alloys containing optimum concentrations of carbon, boron, zirconium, and hafnium; and three alloys having combinations of the elements. Nominal compositions of the alloys are presented in Table II along with the adjusted solution heat treatment temperature for each alloy. Standard creep specimens within 10° of the three major orientations <001>, <011>, and <111> were machined and tested at 1400°F/110 ksi for each alloy. In a few cases, compression specimens were also machined and tested at the same condition. In addition, the temperature dependence of the yield strength was determined for several alloys.

Table II. Composition and Heat Treatment Temperatures of Single Crystal Alloys

Alloy	Weight Percent Minor Elements C	B	Zr	Hf	Solution Temperature °F
Mar-M200-NME	-	-	-	-	2300
Mar-M200-C	0.10	-	-	-	2300
Mar-M200-B	-	0.012	-	-	2300
Mar-M200-ZR	-	-	0.018	-	2300
Mar-M200-HF	-	-	-	1.82	2300
Mar-M200-BZ	-	0.095	0.015	-	2300
Mar-M200-CBZ	0.089	0.013	0.032	-	2300
Mar-M200-CBZH	0.14	0.018	0.064	2.07	2300

Base Alloy: Ni-10 Co-9 Cr-12.5 W-1.0 Cb-5 Al-2 Ti (weight %)
Heat Treatment: Sol. Heat Treat 4 hours/air cool + 1975°F/4 hours + 1600°F/32 hours.

Results

The 1400°F creep curves for alloys with individual additions of minor elements are compared in Figures 4(a) through 4(e), and the results for the alloys with a combination of minor element additions are presented in Figures 4(f) through 4(h). From Figure 4, it can be seen that the addition of the minor elements does not alter the behavior of the <001> or the <011> orientations but increases the creep resistance (lower second-stage creep rate) of the <111> orientation. Individual additions of carbon, boron, and zirconium are not very effective in this regard, but the effect of hafnium is very significant. The alloys containing combinations of the minor elements, especially Alloy Mar-M200-CBZH with hafnium (Figure 4h), exhibit increases in rupture life for the <111> orientation to an average of 240 hours compared to 48 hours for the alloy containing no minor elements (Figure 4a).

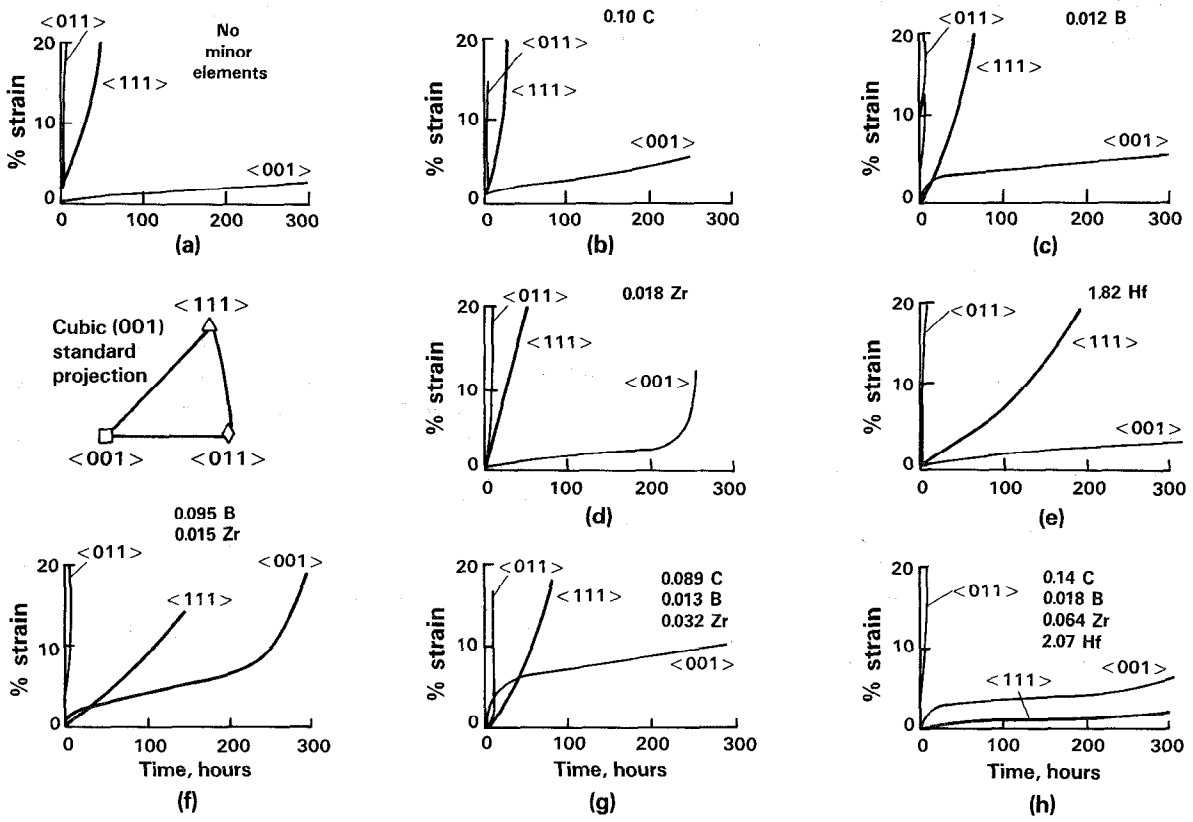

Figure 4 - Effect of minor element additions on 1400°F/110 ksi creep anisotropy of single crystal Mar-M200; (a) no minor elements, (b) to (e) individual additions, and (f) to (h) combination of elements.

In all cases, <001> is observed to be the most creep resistant and <011> the least creep resistant orientation in tension. Differences in rupture life are observed to be very significant, being less than 10 hours for the <011> oriented specimens in contrast to over 300 hours for the <001> oriented specimens in most cases. However, the tensile creep behavior for the two orientations is completely reversed in compression, as shown in Figure 5 for the alloy with no minor elements and Alloy Mar-M200-CBZH containing a combination of minor elements. For the alloy with no minor elements, the <011> orientation with the highest creep rate in tension becomes the one with the lowest creep rate in compression and vice versa for the <001> orientation. For Alloy Mar-M200-CBZH, the effect is not as dramatic. However, neither the creep rate, the creep anisotropy, nor the tension compression

asymmetry of the <001> and the <110> orientation are altered by the addition of minor elements. The effect of minor elements is limited to the deformation behavior of the <111> orientation at intermediate temperatures.

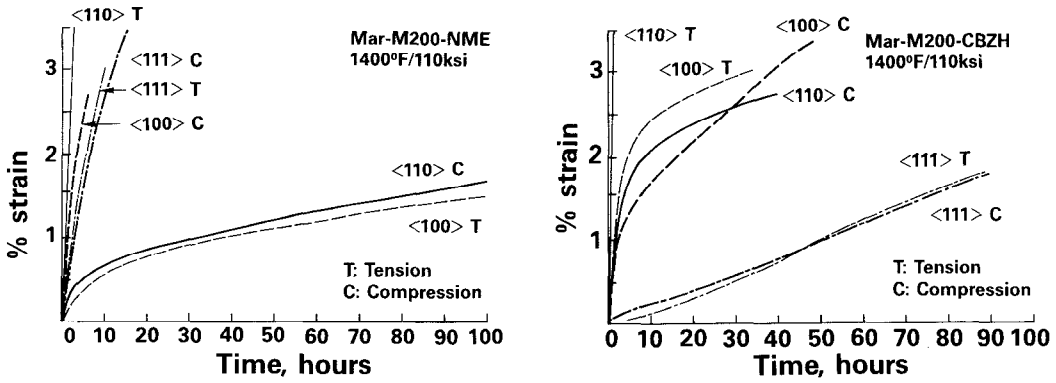

Figure 5 - Observation of tension compression assymetry in 1400°F/110 ksi creep behavior of <100> and <111> orientations for Mar-M200 with and without minor elements.

Discussion of Results

The observed decrease in the creep rate of polycrystalline superalloys with minor element additions, described in Part I, is consistent with earlier work (9). The general validity of the effect for different superalloys and for various combinations of minor element additions indicates the intrinsic difficulty in correlating the effect of minor element additions with microstructural details. In contrast, the parallel between the decrease in the creep rate of polycrystalline alloys (Part I) and the reduction in the creep rate of <111> oriented single crystals (Part II) with the addition of minor elements is very revealing. It points to a common mechanism at least not completely related to grain boundaries. The fact that the base alloy in the polycrystalline study was Alloy 454, and for the single crystal study was Mar-M200, is not relevant. Published results of a 1400°F creep anisotropy study of single crystal alloys CMSX-2 and 454 are comparable to the results presented here for single crystal Mar-M200 containing no minor elements (10).

To understand the effect of minor elements, it is necessary to focus on the deformation behavior of <111> oriented single crystals versus <001> and <011> oriented single crystals. This is well understood for superalloys in terms of octahedral and cube slip behavior as in the case of $L1_2$ compounds (11). Octahedral slip is favored near the <001>-<011> orientations, while cube slip is favored near the <111> orientation as shown geometrically in Figure 6. To what extent cube slip participates in the deformation process depends on alloy composition and temperature, but at higher temperatures, a greater participation of cube slip is well recognized (11). Without going into the details of the cross slip and dislocation core-constriction mechanisms, it is apparent that as the primary effect of the minor elements is on the deformation behavior of the <111> orientation, the minor elements must affect cube slip more than they affect octahedral slip. The deformation behavior of the <001> and <011> orientations, which are predominantly controlled by octahedral slip, are not affected by minor element additions. The observed tension/compression asymmetry in creep, irrespective of minor element additions, is similar to that observed with respect to the yield strength and can be attributed to cross slip and dislocation core-constriction mechanisms associated with octahedral slip which are not available for cube slip (8).

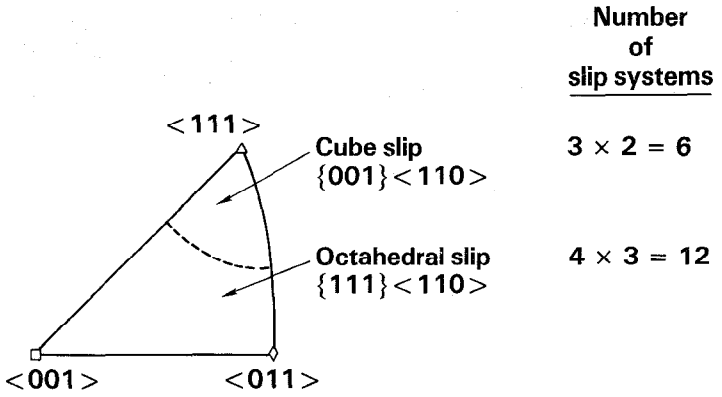

Figure 6 - Relationship between single crystal orientation and operative slip systems in superalloys.

A comparison of the plot of yield strength versus temperature for Mar-M200 with and without minor elements is presented in Figure 7 along with the 1400°F/110 ksi creep curves for the <001> and <111> orientations. For the alloy with no minor elements, the <111> orientation has a lower yield strength and poorer creep resistance. For the alloy with minor elements, both orientations have comparable yield strength and creep resistance.

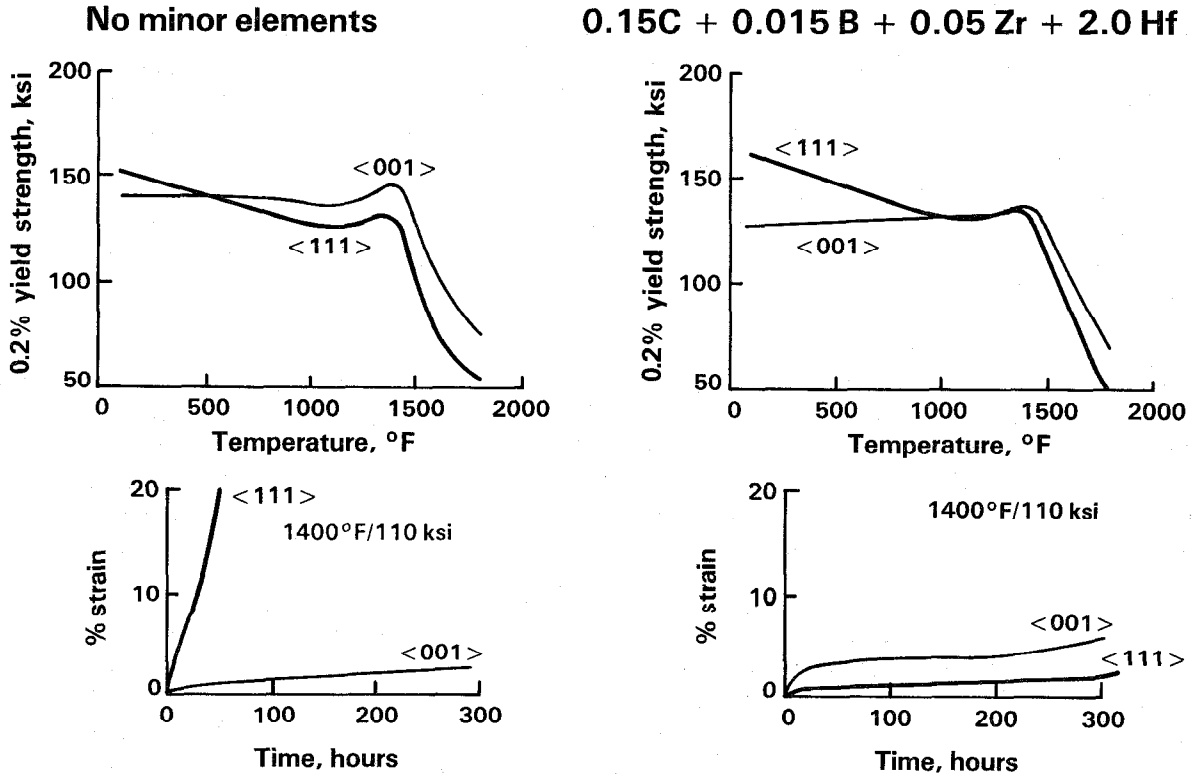

Figure 7 - Comparison of temperature dependence of yield strength and 1400°F/110 ksi creep behavior of Mar-M200 single crystal in <001> and <111> orientations with and without minor elements.

The observation that the minor elements make deformation occurring by cube slip more difficult than that occurring by octahedral slip may be rationalized in terms of an intrinsic dislocation core effect. One does not expect the minor elements to affect the antiphase boundary energy or the stacking fault energy and hence slip on closely packed octahedral planes. However, with the significant difference in atomic size between the minor elements and nickel, the lattice friction is expected to increase and hence slip on more widely spaced cube planes should be affected. Addition of minor elements can change the morphology and size of the gamma prime precipitates which can affect alloy properties. Gamma prime rafting has been demonstrated to affect creep anisotropy (12), but such a mechanism is difficult to isolate from an intrinsic effect without further controlled experiments.

To reconcile the results obtained for the polycrystalline and single crystal material, let us approximate a randomly oriented polycrystal as a collection of single crystals. A polycrystalline material is more like a group of <123> oriented grains because this orientation has the highest (i.e., 24) crystallographically equivalent variants. In this orientation, both octahedral and cube slip systems are equally stressed. If cube slip is favored, however, then qualitatively the <123> direction is more like the <111> direction than the <001> direction. In this simplistic model, the decrease in the creep rate for polycrystalline material with minor element additions parallels the decrease in the creep rate for the <111> oriented single crystals. The mechanics of deformation within a grain is not as simple as in the case of an unconstrained single crystal, but the argument seems consistent with the observations. Consistent with the argument, it can be further conjectured that the addition of minor elements improves the intergranular strain compatibility of polycrystalline superalloys by suppressing cube slip with lower multiplicity, thereby promoting octahedral slip with higher multiplicity. With preferential segregation of the minor elements at the grain boundaries, accommodation of localized deformation in the grain boundary is enhanced with increased multiplicity of the slip systems in the regions near the boundaries.

Summary

1. A fifty-fold improvement in intermediate temperature creep rupture life of polycrystalline superalloys is achieved with about a 0.5 atom percent addition of a combination of minor elements, especially with hafnium as one of the minor elements. In an engineering sense, the elongation to failure is not enhanced significantly.

2. Minor element additions significantly enhance the intermediate temperature creep resistance of <111> oriented single crystals which are favorably oriented to deform by cube slip, but have no effect on the creep behavior of <001> or <011> oriented single crystals which are expected to deform by octahedral slip. The <001> and <011> orientations also show a tension/compression asymmetry in creep similar to the observed asymmetry in yield strength.

3. The beneficial effect of minor elements on polycrystalline superalloys and their effect on single crystal superalloys is reconciled in terms of suppression of cube slip with lower multiplicity relative to octahedral slip with greater multiplicity.

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