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The Effect of Thermal Cycling to 1100° C on the Alpha (Mo) Phase in Directionally Solidified $\gamma/\gamma' - \alpha$ Alloys

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THE EFFECT OF THERMAL CYCLING TO 1100° C ON THE ALPHA (Mo) PHASE IN DIRECTIONALLY SOLIDIFIED $\gamma/\gamma'-\alpha$ ALLOYS

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SUMMARY

Specimens of $\gamma/\gamma'-\alpha$ (Mo) eutectic alloy were thermally cycled or isothermally exposed at temperatures of 1075° to 1100° C. Transmission electron microscopy examination of cycled specimens indicated that even an exposure of 10 minutes effected noticeable changes in the shape of the α phase, and that the changes were cumulative as more cycles were added. The cross sections of fine, smooth fibers changed from rectangles to octagons, while lamellae and irregular shapes spheroidized. These effects are attributed to the differences in thermal expansion coefficients between the α phase and the γ/γ' matrix, and to the higher diffusion rates prevailing at elevated temperatures. Where the configuration of the α phase is a simple shape, such as a fiber, increasing the temperature eventually brings about a stress-free interface between the α phase and the matrix by differential thermal expansion. Where the shape of the α phase is more complex, a stressed interface persists to higher temperatures where diffusion produces the more drastic morphological changes.

INTRODUCTION

Nickel base alloys containing 25 to 35 percent (weight percent) molybdenum and 5 to 8 percent aluminum are of a near-eutectic composition. When directionally solidified at a proper rate in a high temperature gradient, the alloys form in-situ strong, ductile, body-centered cubic molybdenum fibers (α phase) in a ductile matrix composed of mixed face-centered cubic γ and γ' phases. Properties for one of these alloys (Ni-32.3Mo-5.7Al) indicate that they may be useful as turbine blades for advanced aircraft engines with metal operating temperatures up to 1100° C (refs. 1 and 2).

The turbine blades of aircraft engines undergo numerous cycles of heating and cooling. Many turbine blade materials, when subjected to thermal cycling, undergo changes in microstructure, which will adversely affect their mechanical properties (refs. 3 to 5). In directionally solidified eutectic alloys, thermal cycling can cause changes in the microstructural appearance of the reinforcing phases (refs. 6 to 8). In the case of the $\gamma/\gamma'-\alpha$ alloys, various effects have been reported. Spheroidization of the α phase was reported by Woodford (ref. 9), who used specimens with slowly solidified, well aligned fibers, and subjected them to cycles with 4 minutes of heating at 1075° C. Smeggil (ref. 10), who exposed specimens with apparently not well aligned α phase to cycles of 55 minutes at 1150° C, also reported spheroidization of the α phase. However, Henry et al. (refs. 1 and 2), reported no changes in the morphology of apparently well aligned molybdenum fibers after 150 cycles to 1150° C with 50-minute exposures, but noted that stress rupture life decreased, and particulary so in specimens with poor phase alignment.

In view of these data, the present study was undertaken to determine, by optical and electron microscopy examination, whether the α fibers in the directionally solidified γ/γ'-α eutectic alloys are inherently unstable in thermal cycling to near 1100° C, and whether the quality of the alignment is a factor in the stability of the α phase.

EXPERIMENTAL PROCEDURE

Materials

The Ni-33Mo-5.7Al, γ/γ'-α alloy (ref. 1) was used for the majority of the tests in this study. A few specimens of the Ni-30Mo-5.9Al-1.65V-1.2Re composition (ref. 2) were used for comparative purposes. Mastermelts of the compositions were prepared from elemental high purity constituents and cast into remelt bars. Directional solidification of 12.5 mm diameter bar specimens was performed in a modified Bridgman furnace previously described in reference 7, with a gradient of about 250 K/cm at a rate of 20 mm/h. For comparison, some specimens were directionally solidified at 10 mm/h. A flat was ground along the length of every bar, which was then polished and examined metallographically to determine its microstructure. Typical structures are shown in figure 1. They ranged from fibers with near perfect alignment (fig. 1(a)), through various degrees of irregular and lamellar shapes near grain boundaries and within grains (fig. 1(b)), to misaligned and cellular structures (fig. 1(c)). Specimens representing the various structures were selected for cyclic burner rig, cyclic furnace, and isothermal exposures.

Thermal Exposure

Thermal cycling was achieved by two methods. In the first, specimens were exposed for 4 minutes per cycle in a Mach 0.3 burner rig to jet fuel combustion products, and then cooled in an air blast. The specimens reached 1100° C and remained at this temperature for 2 minutes. Exposures totaled between 500 and 1000 cycles. The apparatus used is described in detail in reference 11. In the second, the specimens were exposed 1000 times in a convective air furnace for 5 minutes per cycle (ref. 12). These specimens reached and remained at 1075° C for 3 minutes, and were then cooled in still air for 5 minutes. For comparison, control specimens were exposed isothermally in a furnace for 100 hours at 1100° C, while parts of one specimen were exposed to one and five cycles of 10 minutes at 1100° C, each followed by an oil quench.

Metallography

Microstructures were examined by light optical microscopy and by scanning and transmission electron microscopy. Metallographic examination centered on observation of the α phase. All optical examinations were made on unetched specimens. Specimens for scanning electron microscopy were deep-etched in hydrochloric acid containing a small amount of hydrogen peroxide, to remove the γ and γ' phases, without attacking the α phase. Transmission electron microscopy specimens were thinned electrolytically to less than 0.1 μm in a methanol solution containing 7 percent perchloric acid and 20 percent butanol.

RESULTS AND DISCUSSION

Specimens of the three variations in phase alignment, shown in figure 1, suffer varying degress of degradation after thermal cycling, as illustrated in figure 2. The well aligned fibers, figure 1(a), survived the cycling intact, although occasional fibers show degradation, figure 2(a). Less perfect fibers and lamellar strips, such as can be found near grain boundaries, figure 1(b), have undergone complete spheroidization, figure 2(b). Cellular structures, figure 1(c), showed complete spheroidization, figure 2(c). No difference in effects was observed between specimens of the two compositions, directionally solidified at either 10 or 20 mm/h, nor between those exposed to convective furnace or burner rig cycles.

Light optical microscopy examination of the specimens, exposed isothermally at 1100° C for 100 hours showed that the original α phase structure remained intact, whether or not it was in the form of well aligned fibers, see figure 3. These isothermal results are consistent with those of a previous investigation (ref. 13), where no degradation of ejther well or poorly aligned fibers was observed in a 1-hour exposure to 1245° C. Also, fibers were reported to be unaltered after a 1000-hour isothermal exposure to 1100° C, although some γ and γ' agglomeration and a loss of stress rupture life were observed (ref. 2).

While light optical microscopy is an adequate method to show gross changes in the α phase morphology, examination at higher magnification is required to show the subtle effects of exposure into the 1100° C range. As-directionally solidified fibers are shown in the transverse cross-sections in figure 4. The transmission electron micrograph, figure 4(a), shows fibers of rectangular shape with sharp corners in a γ/γ' matrix. The matrix contains numerous dislocations. The fibers in the scanning electron micrograph, figure 4(b), viewed in perspective, display sharp right-angled corners corresponding to the sharp corners of figure 4(a).

After five cycles of 10 minutes to 1100° C, all the right-angled corners have become truncated, figure 5(a). The effect was evident even after only one thermal cycle (figure not shown). The truncation of the fiber corners is accompanied by an apparent decreased density of dislocations in the matrix and the appearance of an unidentified precipitate in the fiber (compare fig. 5(a) with 4(a)). Precipitates had previously been observed by Pearson and Lemkey after 600 hours of exposure to 1038° C (ref. 14). After 1000 cycles, the truncation of the corners is very evident (compare fig. 5(b) with 4(b)).

Within each grain, all fibers display the same spatial orientation. The fiber surfaces are smooth and uniform, unless there were mechanical or thermal disturbances during the solidification process. The lengths of the fibers are indefinite, but limited by the boundaries of the grain in which they were grown. In well aligned structures, fibers commonly terminate as fine lamellae along these boundaries (figs. 1(b) and 6(a)). As already shown by light microscopy in figure 2(b), such lamellae spheroidize in thermal cycling. Scanning electron microscopy shows the extent of degradation at the grain boundary of a specimen after 750 cycles (fig. 6(b)).

It is evident that the morphology of the α phase in as directionally solidified γ/γ'-α eutectic alloys is metastable. Even a single excursion into the 1100° C temperature range affects the contours of well aligned rectangular α phase fibers. This effect becomes more obvious with thermal cycling, expecially when the alignment or configuration of the α phase is less than ideal.

Considering the observations made in this study and those reported in the literature, a model is proposed to explain the thermally induced changes of the α phase morphology and their dependence on the as-solidified quality of α phase alignment. The model evokes, at low temperatures, elastic strains locked in by cooling from the solidification temperature, and, at high temperatures, diffusion across the matrix -α phase interface. Interphase strains arise from the difference in thermal expansion coefficients between the α phase and the γ/γ' matrix (6.7, 18.3, and 15.5, $X10^{-6}$ K^{-1} between 300 and 1250 K for α, γ and γ', respectively, ref. 15).

The proposed model is illustrated in figure 7. When the alloy cools from solidification S (about 1300° C) to T_{min}, it contracts along line SE. If the matrix alone underwent this cooling, it would contract along a line SM. The α phase, alone, would contract along a line SA, due to its lower coefficient of expansion (contraction) (ref. 15). The difference in coefficients of thermal expansion produces triaxial strains between the matrix and the α phase, so that at T_{min} the α phase is in compression and the matrix in tension (sketch 1). These strains are partly elastic and partly plastic, as indicated by EM' and M'M for the matrix and EA' and A'A for the α phase, respectively.

When the eutectic alloy is reheated to T_{max}, it will expand along line EK. The expansions of the matrix and the α phase, however, first act to relieve the elastic strains. Thus, the matrix will expand as if along a line M'K, which parallels the thermal expansion line MS, and the α phase as if along a line A'L, paralleling AS. Note that lines M'K and A'L cross at a point O. At this point, the locked in elastic strains should be relieved and a stress-free interface exist between the matrix and the α phase (sketch 2). The model proposes that the bond between the α phase and the matrix is principally mechanical. Thus, a stress-free interface is more readily achieved when the interface is smooth and uniform, as with well aligned fibers. As the temperature continues to rise to T_{max}, the cohesive forces between the α phase and the matrix should become too weak to effect a stress reversal and, therefore, separation between the α phase and the matrix may result. In the absence of a stressed interface, only minor morphological changes should occur in the α phase, such as rounding and eventual truncation of the right-angled fiber corners at 1100° C (fig. 5).

The model also proposes that when the α phase is present in more complex shapes, such as coarse, irregular fibers or lamellae, mechanical locking could cause a stressed interface to persist to higher temperatures (greater than T_0). Since the stress-assisted diffusion across the interface would be occurring at high rates, drastic morphological changes would result, as shown in figures 2(b), 2(c), and 6(b).

In thermal cycling, each cooling event should restore the previously described triaxial strain conditions between matrix and α phase, and each heating event should repeat the pseudo-expansions along lines M'K and A'L. This is why thermal cycling can change the shape of α phase cellular structures and imperfectly formed fibers. It should also be recognized that stress-free interface conditions at elevated temperatures, where diffusion rates are high, can be suppressed by imposing an applied stress on the alloy. Then, even well aligned, uniform α fibers will spherodize, as is shown in the elongated and necked regions of specimens failed in stress rupture at 1038° C (ref. 16).

The results obtained in this investigation generally agree with the findings obtained previously. However, in order to predict the response of

α fibers to thermal cycling, it is necessary to examine their shapes at high resolution. Without knowledge of the exact shape of "well aligned" fibers, it is not possible to reconcile all the different effects of thermal cycling discussed in the INTRODUCTION (refs. 2, 9, and 10).

It should be noted that, on the basis of experiments performed here and the information available elsewhere, no temperature has been determined below which fiber stability is assured. The experiments of Woodford, who reported spheroidization at 1075° C (ref. 9), and of Pearson and Lemkey, who encountered morphological changes at 1038° C (refs. 14 and 16) seem to point to a temperature about 1000° C. At lower temperatures, diffusion rates may be too slow to affect the structure. One should also question whether fine, well aligned fibers can survive cycling to well above 1100° C.

CONCLUDING REMARKS

The data reported here raise disturbing questions that must be answered for a successful application of fiber reinforced directionally solidified eutectic superalloys. Microstructural stability should be foremost in the mind of the user, for it will determine the residual properties of the alloy. The user of the γ/γ'-α eutectic alloy must realize that no directionally solidified part will be absolutely perfect and contain only straight fibers with rectangular cross-sections. There may be lamellae at the grain boundaries, and occasional areas where the configuration of a part promotes imperfect alignment characteristics during solidification. These areas will be the ones to undergo the most severe microstructural change and are most likely to show property losses. It would seem appropriate that the mechanical property testing at conditions other than "as-directionally solidified" be emphasized for eutectic alloys. Special attention should be paid to these alloys in the fully processed (such as coated) condition and after repeated exposures to the expected maximum stress and temperature at which parts fabricated from them would operate. Careful microstructural observation at high magnifications should be employed to determine the temperature at which the fully processed alloy is safe to use.

The author recognizes that further research is advisable to substantiate the mechanism proposed for morphological changes of the α phase. In particular, such work should scrutinize the nature of the interface between the α phase and the matrix over a wide range of temperatures. It should determine whether the bond between the phases persists at elevated temperatures where expansion has relieved the stresses which force the phases against each other, or whether the bond is principally mechanical, as proposed for the model. This would greatly contribute to our understanding of the behavior of directionally solidified superalloys and could promote their successful use in many applications.

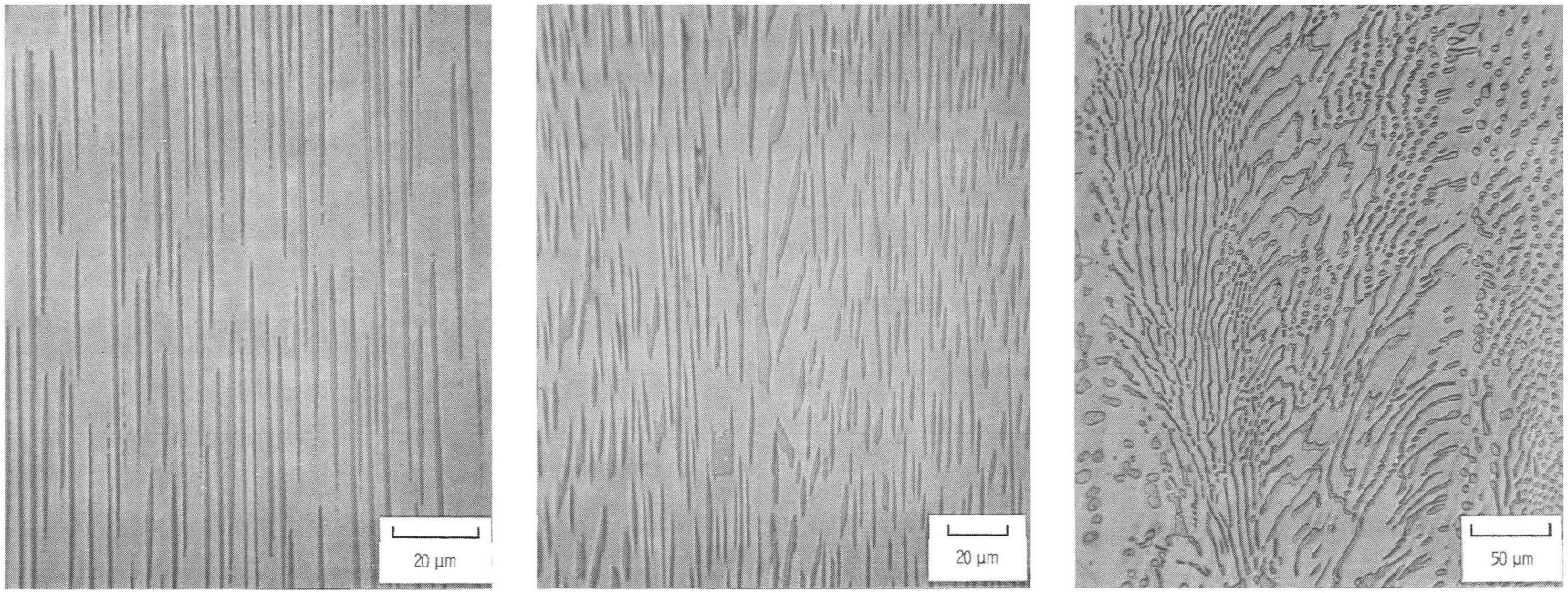
SUMMARY OF RESULTS

The objective of this study was to determine the stability of α fibers in directionally solidified γ/γ'-α eutectic alloys during thermal cycling to about 1100° C, and to so resolve conflicting data reported in the literature. Specimens of the Ni-Mo-Al eutectic alloy were directionally solidified and then exposed to from one to 1000 cycles at about 1100° C. It was observed that:

1. The α phase, when cycled to 1100° C tended to behave as follows:
   a. Well aligned α fibers of uniform rectangular cross-sections maintained their continuity, but their cross-sections changed from rectangles to octagons.
   b. Lamellar and cellular structures spheroidized.
2. The extent of change in shape of the α phase was limited for each single cycle, but appeared to be cumulative as more cycles were imposed on a specimen.
3. The quality of the as-directionally solidified α phase, rather than the rate of solidification or the composition of the alloy, was found to determine the stability of the alpha phase.

REFERENCES

1. M. F. Henry, M. R. Jackson, and J. L. Walter, SRD-78-198, General Electric Co., Schenectady, NY, April 1978. NASA CR-135151.
2. M. F. Henry, M. R. Jackson, M. F. X. Gigliotti, and P. B. Nelson, SRD-78-191, General Electric Co., Schenectady, NY, January 1979. NASA CR-159416.
3. M. Kaufman, General Electric Co., Cincinnati, OH, December 1974. NASA CR-134791.
4. D. A. Woodford, Mater. Sci. Eng., 1976, vol. 24, pp. 257-273.
5. D. A. Woodford, in Fracture 1977, Advances in Research on the Strength and Fracture of Materials, D. M. R. Taplin, ed., Volume 2B, pp. 803-812, Pergamon Press, New York, 1977.
6. F. M. Dunlevey and J. F. Wallace, Case Western Reserve Univ., Cleveland, OH, September 1973. NASA CR-121249.
7. F. H. Harf, NASA TM X-3434, 1977.
8. W. Kurz and P. R. Sahm, Gerichtet erstarrte eutektische Werkstoffe, pp. 238-240, Springer Verlag, Berlin, 1975.
9. D. A. Woodford, in Conference on In-Situ Composites-III, J. L. Walter, M. F. Gigliotti, B. F. Oliver, and H. Bibring, eds., pp. 410-419, Ginn Custom Publishing, Lexington, MA, 1979.
10. J. G. Smeggil, UTRC/R78-912959, United Technologies Research Center, East Hartford, CT, October 1978. AD-A063570.
11. H. R. Gray and W. A. Sanders, in Conference on In-Situ Composites-II, M. R. Jackson, J. L. Walter, F. D. Lemkey and R. W. Hertzberg, eds.; Xerox Individualized Publishing Company, Lexington, MA, pp. 201-210, 1976.
12. C. A. Barrett and C. E. Lowell, Oxid. Met., 1975, vol. 9, pp. 307-355.
13. F. H. Harf, in Conference on In-Situ Composites-III, J. L. Walter, M. F. Gigliotti, B. F. Oliver, and H. Bibring, eds., pp. 399-409, Ginn Custom Publishing, 1979.
14. D. D. Pearson and F. D. Lemkey, UTRC/78-912834-4, United Technologies Research Center, East Hartford, CT, June 1978. AD-A032642.
15. Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, Thermal Expansion, Metallic Elements and Alloys, Thermophysical Properties of Metals, Vol. 12, IFI Plenum, New York-Washington, 1975.
16. D. D. Pearson and F. D. Lemkey, in Solidification and Casting of Metals, Book 192, pp. 526-532, Metals Society, London, 1979.

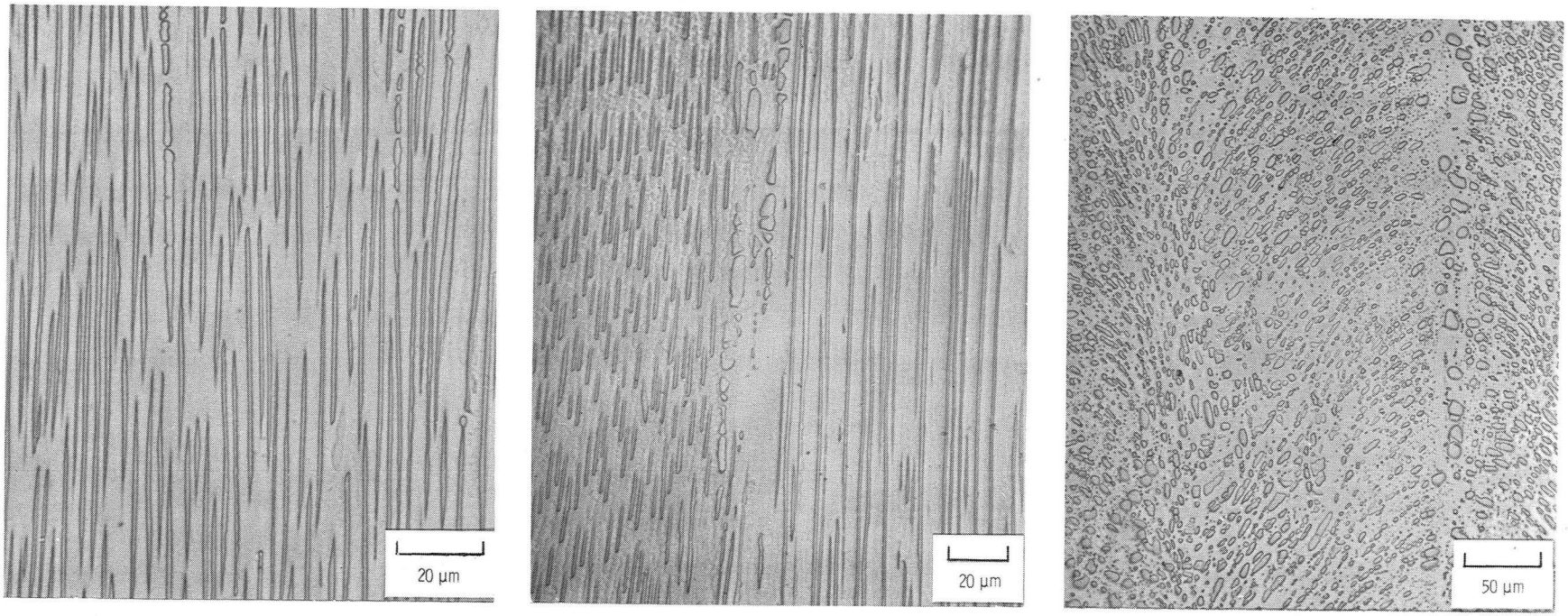


(a) WELL-ALIGNED.

(b) ALIGNED WITH LAMELLAE NEAR GRAIN BOUNDARIES.

(c) CELLULAR.

Figure 1. - Types of α phase alignment in as-directionally solidified γ/γ'-α eutectic alloy. Unetched.



(a) FIBERS INTACT WITH OCCASSIONAL SPHEROIDIZATION.

(b) SPHEROIDIZATION OF LAMELLAE NEAR GRAIN BOUNDARIES.

(c) SPHEROIDIZATION OF CELLUALR STRUCTURES.

Figure 2. - Typical appearance of α phase after cycling directionally solidified γ/γ' - α eutectic alloy up to 1000 times to near 1100° C. Unetched.

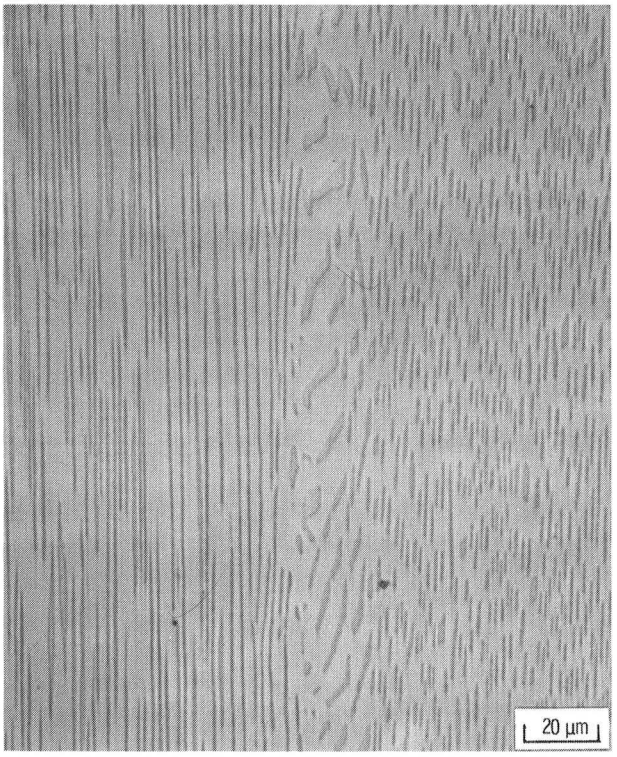
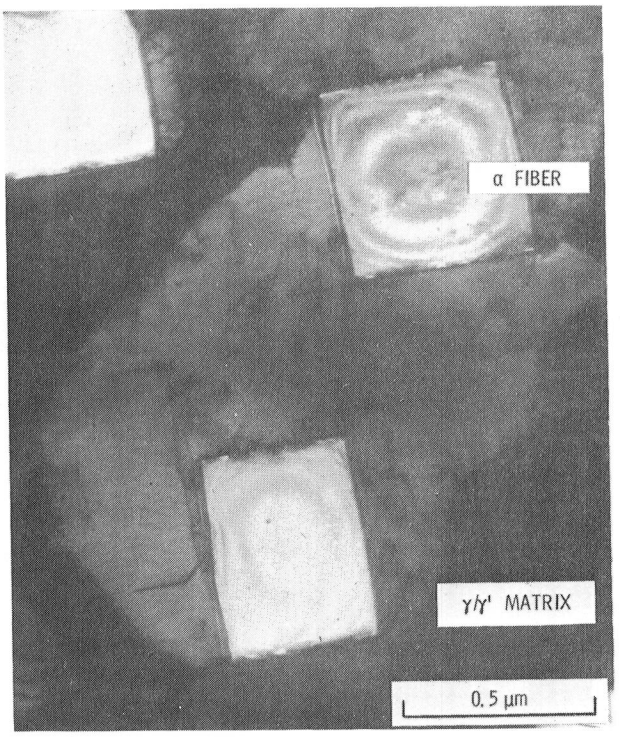
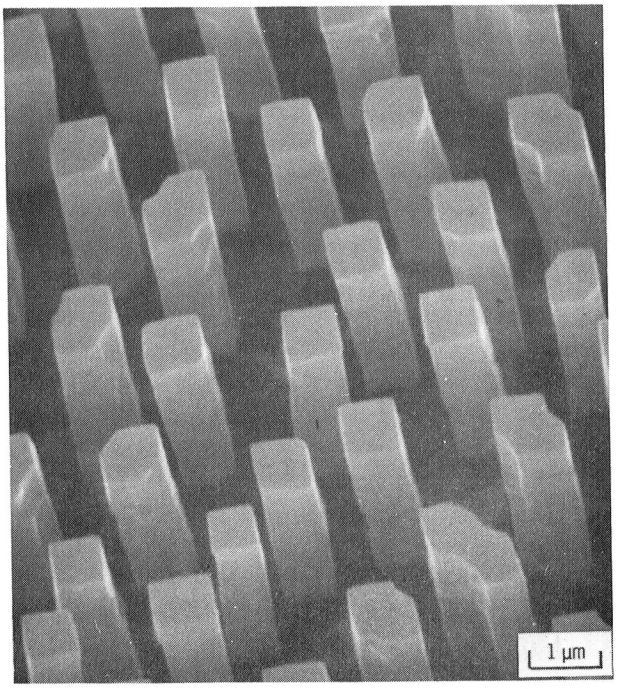


Figure 3. - Directionally solidified $\gamma/\gamma'-\alpha$ eutectic alloy after isothermal exposure of 100 hours at 1100^{0} C. Note absence of spheriodized α phase near grain boundaries as compared with figure 2(b).

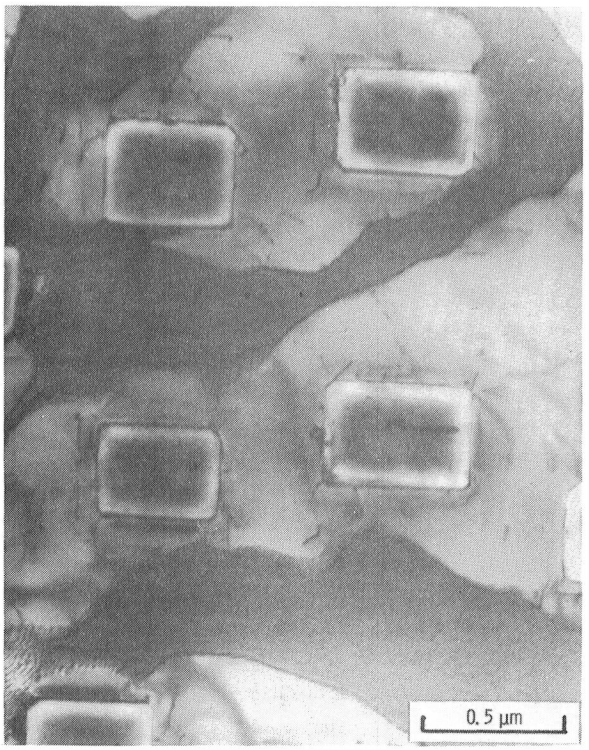


(a) TRANSMISSION ELECTRON MICROGRAPH.

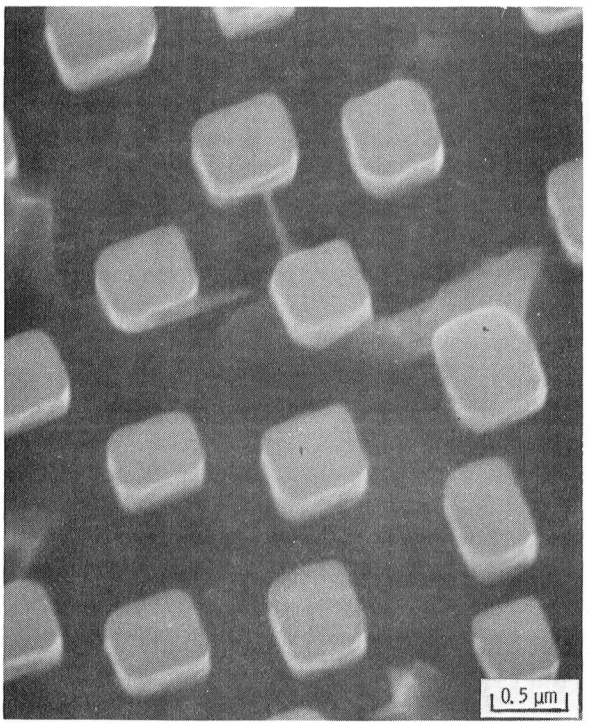


(b) SCANNING ELECTRON MICROGRAPH.

Figure 4. - Cross-sections of as-directionally solidified γ/γ' - α eutectic alloy. The fibers all have sharp right-angled corners.

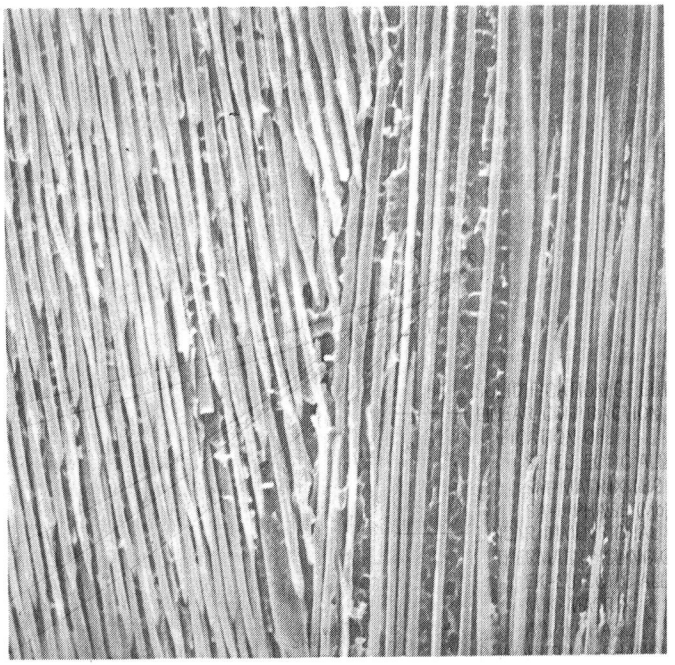


(a) TRANSMISSION ELECTRON MICROGRAPH AFTER 5 CYCLES OF 10 MINUTES AT 1100° C AND OIL QUENCH.

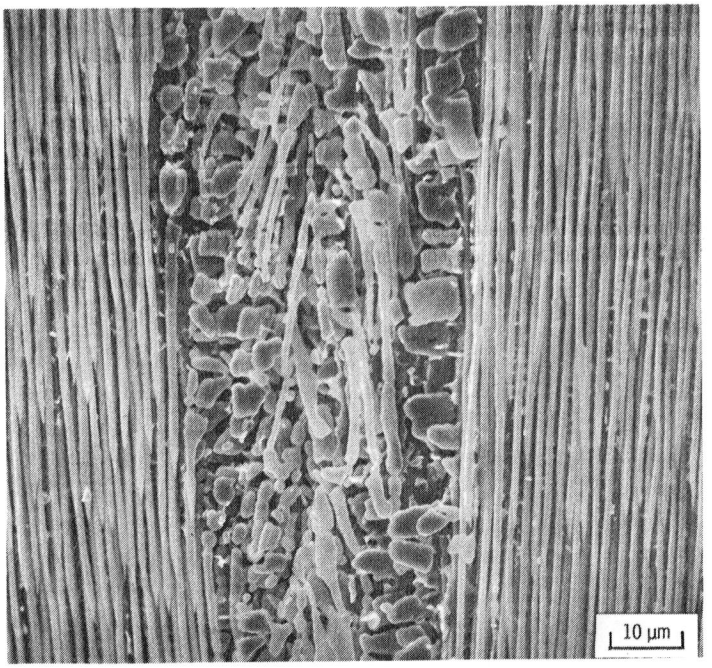


(b) SCANNING ELECTRON MICROGRAPH AFTER 1000 CYCLES OF HEATING 4 MINUTES TO 1100° C IN A BURNER RIG.

Figure 5. - Effect of thermal cycling on α fibers of directionally solidified γ/γ'-α alloy. All corners are truncated and a precipitate is present in the fibers.



(a) AS-DIRECTIONALLY SOLIDIFIED.



(b) AFTER 750 CYCLES OF HEATING 4 MINUTES TO 1100° C IN A BURNER RIG.

Figure 6. - Scanning electron micrographs showing grain boundaries of directionally solidified $\gamma/\gamma'-\alpha$ alloy, before and after thermal cycling to 1100° C.

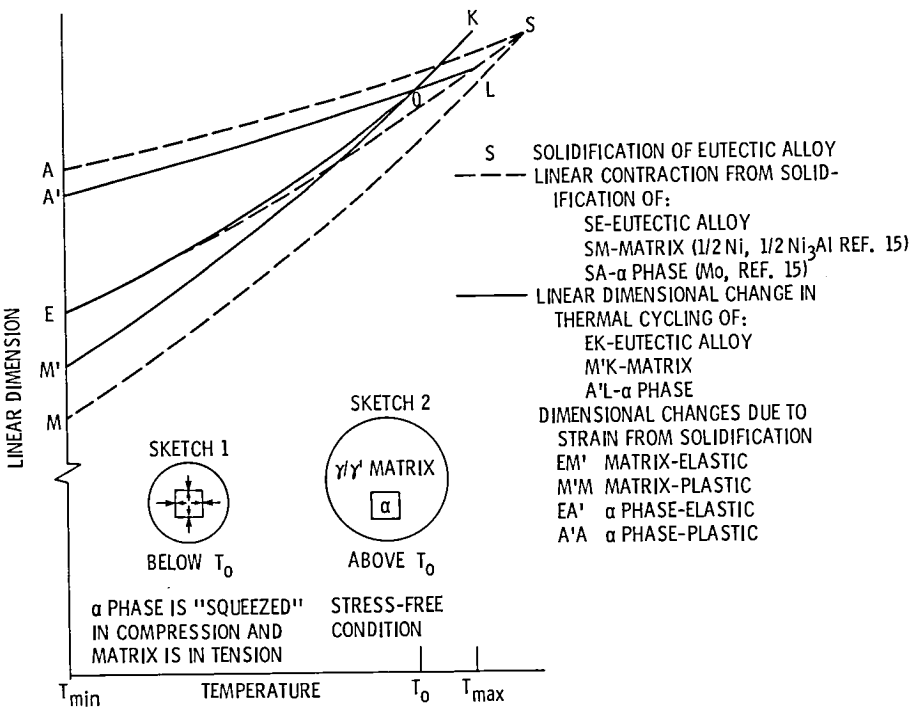


Figure 7. - Schematic representation of the proposed model for the dimensional changes and strains between the γ/γ' matrix and the α phase of a directionally solidified γ/γ' - α eutectic alloy as a function of temperature.

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16. Abstract

In γ/γ'-α eutectic alloys (Ni-Mo-Al), the resistance of the α phase to morphological changes during thermal cycling was found to be dependent on the structure formed during directional solidification. Fine, smooth α fibers survived up to 1000 five-minute cycles to 1100° C with minor microstructural contour changes, while coarser and irregularly shaped α fibers tended to spheroidize. A mechanism to explain this phenomenon is proposed. It is suggested that on heating to 1100° C, the α phase is likely to undergo morphological changes, until differential thermal expansion creates a stress-free interface between the α phase and the γ/γ' matrix.

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