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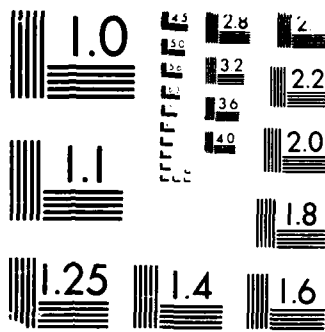
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Annual Technical Report on
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Increased Stiffness RSP Aluminum Alloys

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SUMMARY

The objective of this research is to investigate two promising systems as the basis for high temperature aluminum alloys useful to 425°C (800°F). The first is a metal matrix composite consisting of an aluminum-magnesium alloy matrix reinforced by spinel (magnesium aluminate) particulate. The second system is tri-aluminum (zirconium, vanadium) dispersed in aluminum matrix. Here the lattice parameter matches that of the matrix. Research on dilute alloys has shown a low coarsening rate for this intermetallic at 425°C. Study of more concentrated alloys is underway.

A mechanical alloying-liquid metal infiltration procedure for preparing specimens of the aluminum alloy matrix-spinel composite has been worked out and specimens with 4 vol.% spinel have been prepared. Also, 4 vol.% alumina composite samples were prepared for comparison. Spinel particles were within the aluminum alloy grains in contrast to the alumina which was at grain boundaries. The spinel composite had much better creep resistance at 410°C.

Extrusions containing 5 vol.% tri-aluminum (0.75 vanadium, 0.25 zirconium) were prepared for this research by Lockheed-Palo Alto from rapidly solidified foil. The measured creep rate at 425°C is much lower than in the current aluminum-iron-cerium alloy. An aluminum-vanadium intermetallic compound, however, forms at grain boundaries leading to a precipitate free zone which grows slowly at 425°C.

STATEMENT OF WORK

By analogy with Ni-base superalloys which are useful to $0.75 T_m$ (T_m is the absolute melting temperature of Ni), one may anticipate development of an Al base alloy useful to approximately 425°C or 800°F . In order to develop a successful Al alloy for use at such a temperature, many basic principles must be considered. It is proposed that such an alloy will owe its strength at high as well as room temperature to a uniform dispersion of second phase particles which are coherent or semi-coherent with the matrix. To test this theory, two systems are under study:

1. Al-Mg alloy matrix - MgAl_2O_4 composite
2. Al- $\text{Al}_3(\text{Zr},\text{X})$ dispersions

Both of these systems were selected on the basis of lattice matching between an Al alloy matrix and the dispersed phase. Preliminary work was done on Al- Al_3Zr and Al- $\text{Al}_3(\text{Zr},\text{V})$ under AFOSR Grant No. 82-0005 where the results on dilute alloys were very promising. Current research on Al-5 vol.% ($\text{Zr}_{.25}\text{V}_{.75}$) shows great promise; however, incoherent Al_{10}V was found to form on grain boundaries in the more concentrated alloy which leads to a precipitate free zone which increases in width on aging. Therefore, research has begun on Al-Zr-Ti alloys which won't have this problem.

PROGRESS AND RESULTS

1. Al-Mg alloy matrix- MgAl_2O_4 spinel composite

The cubic spinel, nominal composition MgAl_2O_4 , appears to be a better candidate oxide for the dispersion strengthening of Al than the hexagonal oxide $\alpha\text{-Al}_2\text{O}_3$. The lattice parameter of stoichiometric MgAl_2O_4 is 8.083\AA which is almost twice that of Al, 4.0496\AA . Thus a semicoherent interface may be anticipated. Furthermore, at least one spinel-structured oxide

exhibits some ductility at room temperature.² If the dispersed spinel particles in the Al alloy matrix have even very limited ductility, this should result in a much better fracture toughness than with particles like α -Al₂O₃ or SiC which behave in a very brittle fashion. Since the elastic constants of spinel are considerably larger than those of Al, improved stiffness as well as improved high temperature strength is expected from dispersing spinel in an Al alloy matrix.

To date a procedure for preparing creep and elevated temperature fatigue specimens of Al-Mg alloy matrix-spinel (MgAl₂O₄) or corundum (α -Al₂O₃) dispersions has been developed. Al-3% Mg rapidly solidified powder for the matrix was kindly provided for this research by the Alcoa Technical Center. Commercially available spinel and α -Al₂O₃ powders were provided by Baikowski. Composites containing 4 vol.% of either oxide were prepared by mechanical alloying with 1 wt.% oleic acid as a "grinding" aid using alumina pellets as the "grinding" medium. The mechanically alloyed powders were cold pressed to 0.75 in diameter discs with a dual action die at 350 MPa pressure. The cold pressed pellets and dies were heated to 710°C for 5 minutes for liquid metal infiltration and then pressure forged in a platen press heated to 140°C to form discs 20 mm diameter and 2 mm thick. The pressure forged discs were then cold rolled to 0.8 mm thickness with intermediate anneals at 600°C. The final densities were in the range 99 to 100% of the theoretical. The specimens were cut using electro-discharge machining.

Transmission electron microscopy showed that a much better dispersion of spinel particles in the Al-3% Mg matrix was achieved than with α -alumina. The former were dispersed within grains while the latter were at grain boundaries having pinned them during recrystallization. This in itself may

be an indication that the matrix/spinel interface has lower interfacial energy than the matrix/ α -alumina interface within grains. The alumina particles (150-300 μm diameter) were much larger than the spinel particles (30-150 μm). The former were not reduced in size by the mechanical alloying. However, in both cases the distribution of particles was uneven. This resulted in uneven grain size.

Tensile tests were conducted at room temperature and creep tests at 410°C. The ultimate tensile stress of the Al(3% Mg)-4 vol.% spinel was 235 MPa while the elongation to fracture was 15%. For Al(3% Mg)-4 vol.% α -alumina, the UTS was 210 MPa with 9% elongation to fracture. Better properties can no doubt be achieved with more uniform particle dispersions and smaller particle size with α -alumina. The desired high strengths will require higher volume fraction of particles.

The creep results at 410°C are summarized in Table 1.

TABLE 1.
Steady state creep data for Al(3% Mg)/4 vol.% spinel
and Al(3% Mg)/4 vol.% α -alumina metal matrix composites

Stress MPa	Strain Rate (sec^{-1})	
	Al-spinel	Al-alumina
17	-	1.3×10^{-5}
22	2×10^{-6}	26×10^{-6}
30	105×10^{-6}	990×10^{-6}
35	624×10^{-6}	-

The creep resistance of the Al-spinel MMC at 410°C is clearly better than the Al-alumina MMC. This is at least in part due to the better more uniform particle dispersion achieved with the latter.

Future research will be focused on achieving better particle dispersions and on preparing and testing MMC samples with higher volume fraction of dispersed phase.

2. Al-Al₃(V,Zr) dispersions

In the previous studies on this system reported in the previous annual report, a remarkably slow volumetric coarsening rate of $1.0 \times 10^{-28} \text{ m}^3/\text{h}$ at 425°C was found for the metastable cubic $L1_2$ structured $\text{Al}_3(\text{Zr}_{.25}\text{V}_{.75})$ in 5 vol.% precipitate melt spun ribbons (alloy No. 4). However, a region deplete of $L1_2$ precipitates, i.e., a precipitate free zone (PFZ), formed along the grain boundaries during aging due to formation of the stable phases. It was also found that the PFZ width increased with aging time. In order to understand the growth mechanism for the $L1_2$ phase as well as that for the PFZ, detailed studies of the same ribbons, i.e., Al-5 vol.% $\text{Al}_3(\text{Zr}_{.25}\text{V}_{.75})$ alloy, aged at different temperatures were undertaken.

Figure 1 shows the coarsening results of the $L1_2$ precipitates at 425, 450 and 500°C , where the cube of the average particle radius, \bar{r} , is plotted against aging time, t . The linear correlation coefficient, R , and the slope for each best fitting line are given in Table 2. A linear relationship between the cube of \bar{r} and t seems well satisfied. An LSW volume diffusion controlled process described by Eq.(1) seems to be the growth mechanism for the $L1_2$ structured $\text{Al}_3(\text{Zr}_{.25}\text{V}_{.75})$ precipitates.

$$\bar{r}_t^3 - \bar{r}_0^3 = \frac{12.8\sigma D V_m^2 C}{9RT} t = Kt \quad (1)$$

Taking the logarithm from both sides of Eq.(1), the activation energy for the particle coarsening, Q_c , can be calculated from the plot of $\ln(KT/V_m^2 C \sigma)$ vs. the reciprocal of RT . To a first order approximation, the factors C_∞ , V_m and σ are assumed to be constant in the temperature range from 425°C to 500°C . This is a good assumption for the last two terms. Then, Q_c is calculated to be 294 KJ/mole. This value is closer to

the activation energy for diffusion of Zr in Al than that for V, 242 and 82 KJ/mole respectively. Consequently, the volume diffusion of Zr is thought to be the rate controlling process for the Ostwald ripening of the $L1_2$ phase. Furthermore, Q_c is corrected to 230 KJ/mole after considering the temperature dependence of C_∞ . This value is even closer to the activation energy for Zr diffusion in Al. In the above calculation, C_∞ was taken from the solvus line of the stable Al_3Zr , DO_{23} structured phase, even though it is expected to be somewhat different from that of the $L1_2$ phase. The latter is not accurately known at this time. Nevertheless, the above results are self-consistent suggesting that the coarsening kinetics of the $L1_2$ phase is an LSW volume diffusion controlled process.

The growth kinetics of the PFZ at 425, 450 and 500°C were investigated and the results are summarized in Fig. 2 where the PFZ half-width, $W_{PFZ}/2$, is plotted vs. square root of the annealing time as done by Jensrud and Ryum¹ for Al-Li alloys. According to them, the growth behavior of the PFZ in an Al-Li alloy which has a similar microstructure to the present Al-Zr-V alloy can be described by the following equation,

$$W_{PFZ}/2 = b(Dt)^{\frac{1}{2}}, \quad (2)$$

where D is the diffusivity of solute in Al and b is a complicated function of the alloy composition and the solute contents in the Al matrix adjacent to the both sides of the PFZ.¹ Using the same procedure as done previously for coarsening of the $L1_2$ phase, the activation energy for the PFZ growth is calculated to be 285 KJ/mole by taking b as a constant since it is only a slowly varying function of the solute concentration in the Al matrix in the temperature range concerned here. The calculated activation energy indicates that PFZ growth in the present alloy is also controlled

by the volume diffusion of Zr, not V, in the Al matrix. The grain boundary precipitates are, however, mainly $Al_{10}V$. A possible explanation is given as follows. Since V diffuses faster than Zr in Al at the aging temperature, as soon as Ll_2 particles dissolve, vanadium diffuses toward the grain boundaries and it leaves a local matrix with a high Zr content behind. The further dissolution of other Ll_2 particles will be retarded until this excess of Zr diffuses to the grain boundaries to form Al_3Zr or to partition into the $Al_{10}V$ as a solute. As a result, the final growth rate of PFZ is then determined by the volume diffusion of Zr in Al. This leads to the promising result that the PFZ will grow only slowly at the application temperature of interest for this alloy.

In the present alloy, most of grain boundary precipitates are $Al_{10}V$. High resolution transmission electron microscopy (HRTEM), as shown in Fig. 3, disclosed that micro-twins and stacking faults are frequently observed in this phase. The average intercept length, \bar{L} , the volume fraction, ϕ , of the grain boundary precipitates and grain size D after various aging times were measured by quantitative metallography. The results are listed in Table 3. Basically, the volume fraction ϕ increases linearly with square root of aging time. However, since grain size does not increase much, less than a 10% increase after 1200 hours of exposure at 425°C following a preaging at 500°C for 2.5 hours, the $Al_{10}V$ particles forming along the grain boundaries have the positive effect of preventing grain growth.

Figure 4 is an HRTEM image of an Ll_2 particle aged at 600°C for 1.5 hours. The atomic image of the Ll_2 phase is clearly distinguishable from the matrix. The ordered structure of the Ll_2 phase still remains after exposure at this high temperature. It is also shown that the

interface between the $L1_2$ particle and Al matrix is fully coherent. However, a fault structure proven to be an anti-phase domain boundary is formed inside the $L1_2$ particles, as shown in Fig. 5. This anti-phase boundary can be caused by coalescence of two out-of-phase $L1_2$ particles or by the shear produced by a dislocation on $\{100\}$ planes.

The $L1_2$ particles in extruded bars behave similar in their growth kinetics as in the melt spun ribbon at 425°C . The results are shown in Fig. 6 from where a volumetric growth rate of $1.1 \times 10^{-26} \text{ m}^3/\text{h}$ is calculated. It was also found that creep, done at 425°C , increases the growth rate of the $L1_2$ particles by around 50%.

More concentrated Al-Zr-V alloys designed to contain 15 and 25 vol.% $L1_2$ phase made by melt spinning were studied. TEM observations disclosed that a large amount of coarse $Al_{10}V$ particles, around $1 \mu\text{m}$ in size exist in the as-quenched 25 vol.% alloy, which results in the ribbons being brittle after quenching. The 15 vol.% ribbons are ductile even though lots of $Al_{10}V$ phase particles were observed after quenching, but their particle size are generally smaller, around $0.1 \mu\text{m}$. After aging at 500°C , the spherical $L1_2$ phase precipitated out in the 15 vol.% alloy. However, the amount of $L1_2$ phase is less than in the previous 5 vol.% alloy. This is because less solutes remained dissolved in the matrix after quenching. Apparently, a rapid solidification process having a higher quenching rate than the process used at Lockheed in the present study is required to produce a more concentrated and useful alloy.

An error in reporting the creep results was made in the last annual report due to a mixup between alloys 2 and 3. Chemical analyses showed that alloy 2, which has the highest Zr content, actually crept faster than the other two alloys. Figure 7 presents the correct creep results where the

worst test result from each alloy is given. High temperature tensile tests carried out at 425°C reveal that the yield strengths of alloys 2 and 4 are 14 and 40 MPa respectively. Apparently, the poor creep properties observed in alloy 2 are due to its weak strength at 425°C. Detailed microstructural studies found that more coarse equilibrium phase particles, around 1-5 μm in size, are present in alloy 2 than are present in alloys 3 and 4. This is suggested to be one of the reasons why alloy 2 is so weak. The high Zr alloy has a higher melting temperature which makes it more difficult to process by rapid solidification.

It should be pointed out that Al-Mg with 4 vol.% spinel has better creep resistance than the Al-4 vol.% $\text{Al}_3(\text{Zr}_{.25}\text{V}_{.75})$ alloy (alloy No. 4).

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1. O. Jensrud and N. Ryum, "The Development of Microstructures in Al-Li Alloys", *Mat. Sci. Eng.* 64 (1984) 229-236.

LIST OF PUBLICATIONS -- AF SUPPORTED

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2. L. Angers, M. E. Fine and J. R. Weertman, "Effect of Plastic Deformation on the Coarsening of Dispersoids in a Rapidly Solidified Al-Fe-Ce Alloy", *Metall. Trans.* 18A (1987) 555.
3. R. E. Lewis, D. D. Crooks, Y. C. Chen, M. E. Fine and J. R. Weertman, "High Temperature Al-Zr-V Alloys Using Rapid Solidification Processing", *Proc. of 3rd Intl. Conf. on Creep and Fracture of Engineering Materials and Structures*, B. Wilshire and R. W. Evans (eds.) The Institute of Metals, London (1987) pp. 331-346.
4. Y. C. Chen, M. E. Fine, J. R. Weertman and R. E. Lewis, "Coarsening Behavior of Ll_2 Structured $\text{Al}_3(\text{Zr}_x\text{V}_{1-x})$ Precipitates in Rapidly Solidified Al-Zr-V Alloy", *Scripta Metall.* 21 (1987) 1003.
5. Y. C. Chen, M. E. Fine, J. R. Weertman and R. E. Lewis, "A Promising Strengthening Dispersoid for the High Temperature Al Alloy", presented at the 116th TMS Annual Meeting, Denver, Colorado, 1987. Paper in preparation.

LIST OF PUBLICATIONS -- AF SUPPORTED (continued)

6. T. S. Creasy, J. R. Weertman and M. E. Fine, "Al Alloy with Spinel for Oxide Dispersion Strengthening" to be presented (and published) at the TMS Symposium on Dispersion Strengthened Aluminum Alloys to be held in Phoenix, Arizona at the 1988 TMS Annual Meeting 25-29 January 1988. Paper in preparation.
7. M. E. Fine, "Stability and Coarsening of Dispersoids in Aluminum Alloys" to be presented (and published) at the TMS Symposium on Dispersion Strengthened Aluminum Alloys to be held in Phoenix, Arizona at the 1988 Annual Meeting 25-29 January 1988. Paper in preparation.
8. Terry S. Creasy, "Oxide Dispersion-Strengthening of Al-3% Mg with Spinel and Alumina", M.S. Thesis, Northwestern University, Dept. of Materials Science & Engineering, Evanston, IL.

TABLE 2.

Measured coarsening rate constant, K, and coefficient of linearity, R, for $Ll_2 Al_3 (Zr_{.25} V_{.75})$ precipitates at 425, 450 and 500°C.

Temperature (°C)	K (m^3/hr)	R
425*	1.03×10^{-28}	0.997
450*	6.13×10^{-28}	0.997
500	1.28×10^{-26}	0.996

* Specimens were preaged at 500°C for 2.5 hrs. to prevent cellular precipitation.

TABLE 3.

Changes of average intercept length, \bar{L}_3 , volume fraction, ϕ , of grain boundary precipitates, and grain size, D, in alloy 4 ribbon with aging time at 425°C.

Aging Time (hours)	\bar{L}_3 (μm)	ϕ	D (μm)
0	0.18	0.023	3.4
200	0.25	0.031	3.53
400	0.32	0.034	3.7
800	0.34	0.039	3.8
1200	0.35	0.041	4.0

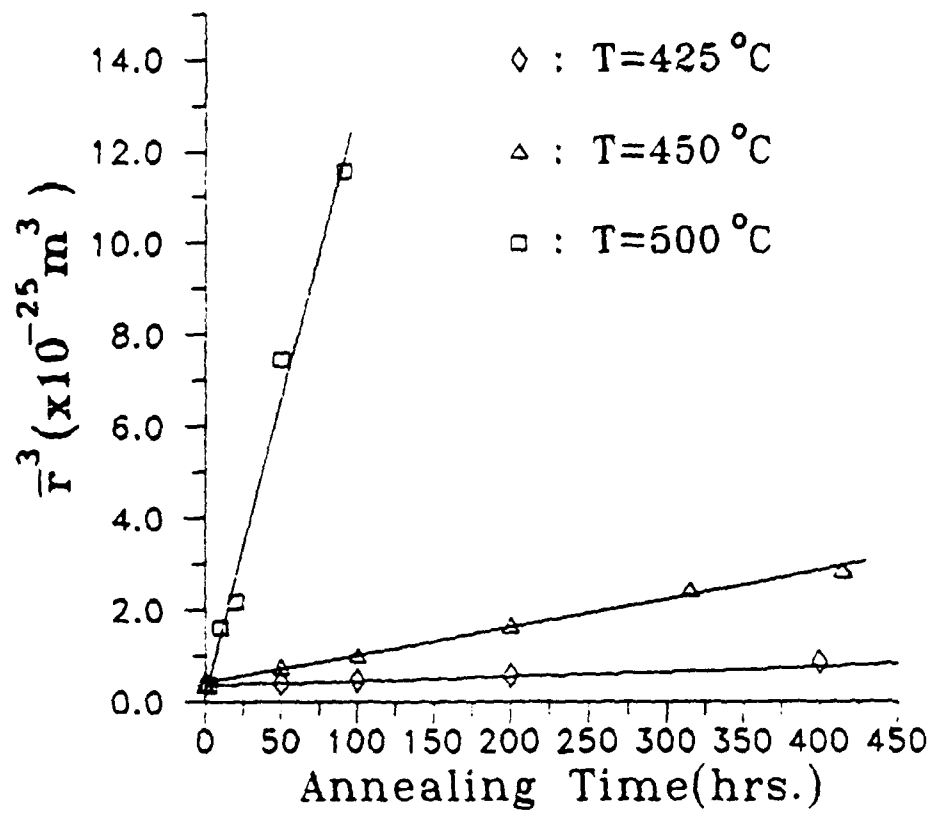


Fig. 1
 Coarsening kinetics of $L1_2 Al_3 (Zr_{.25} V_{.75})$ precipitates at
 425, 450 and 500°C , after a pre-treatment of 2.5 hours at
 500°C in 4 vol.% precipitate alloy (alloy No. 4).

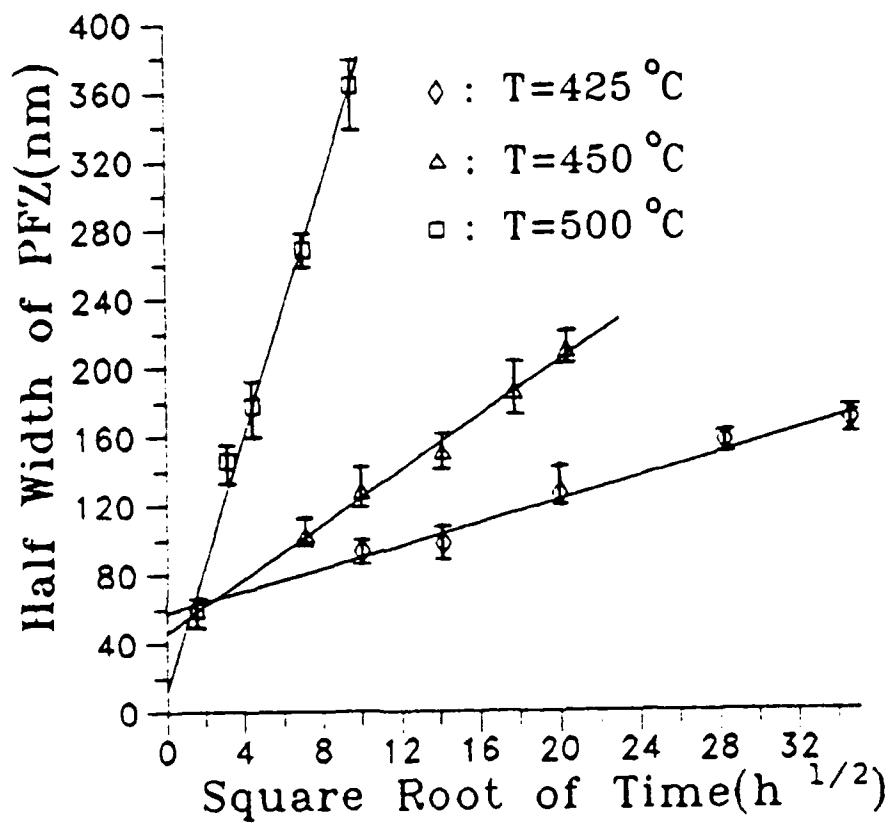


Fig. 2

Growth kinetics of PFZ at 425, 450 and 500°C, after a pre-treatment of 2.5 hours at 500°C (alloy No. 4).



FIG. 3

High-resolution TEM image of grain boundary Al₃V phase, where a micro-twin indicated by letter T and a stacking fault indicated by letter S are observed. It was taken close to (110) zone axis.

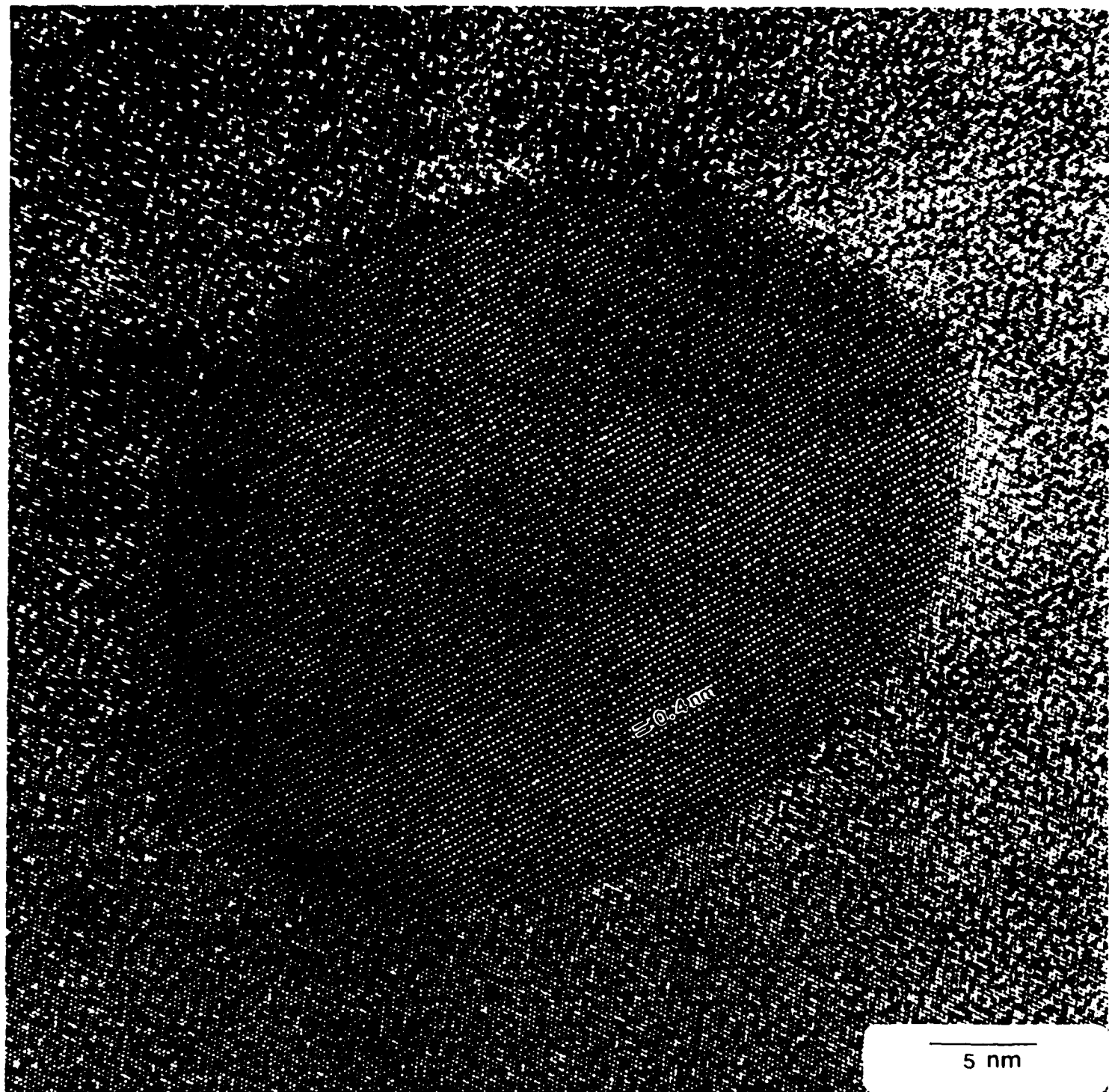


Fig. 4

High resolution TEM image of L₁₂ precipitate, which was taken close to (110) zone axis.

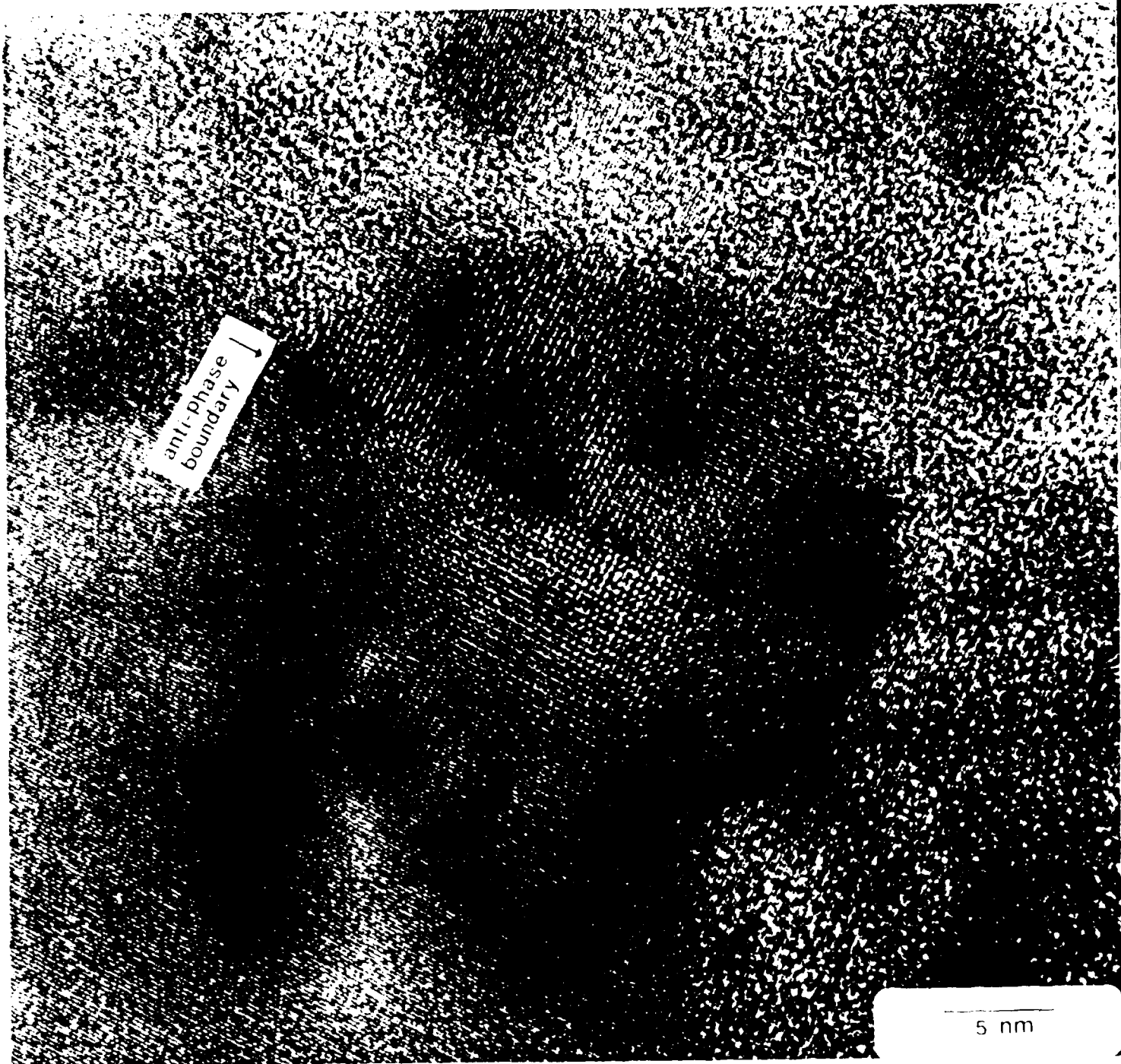


Fig. 1

High-resolution TEM image of Li_2O precipitate, within it an anti-phase domain is present. It was taken along the $[100]$ zone axis.

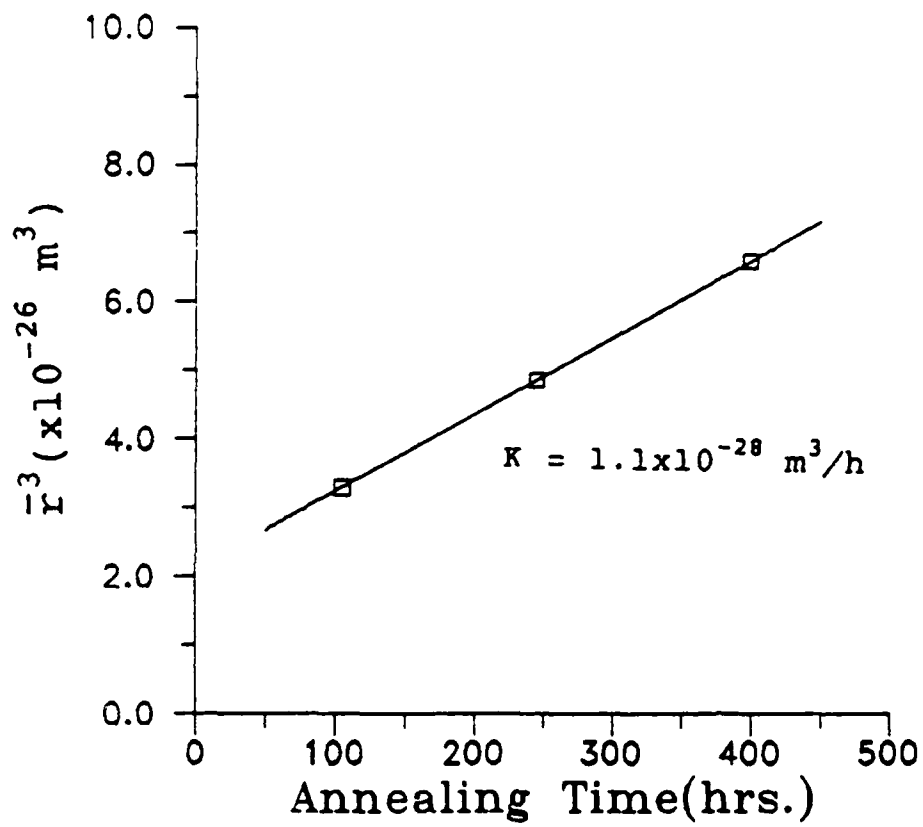


Fig. 6
Growth kinetics of $L1_2$ phase at $425^\circ C$
in extruded bar.

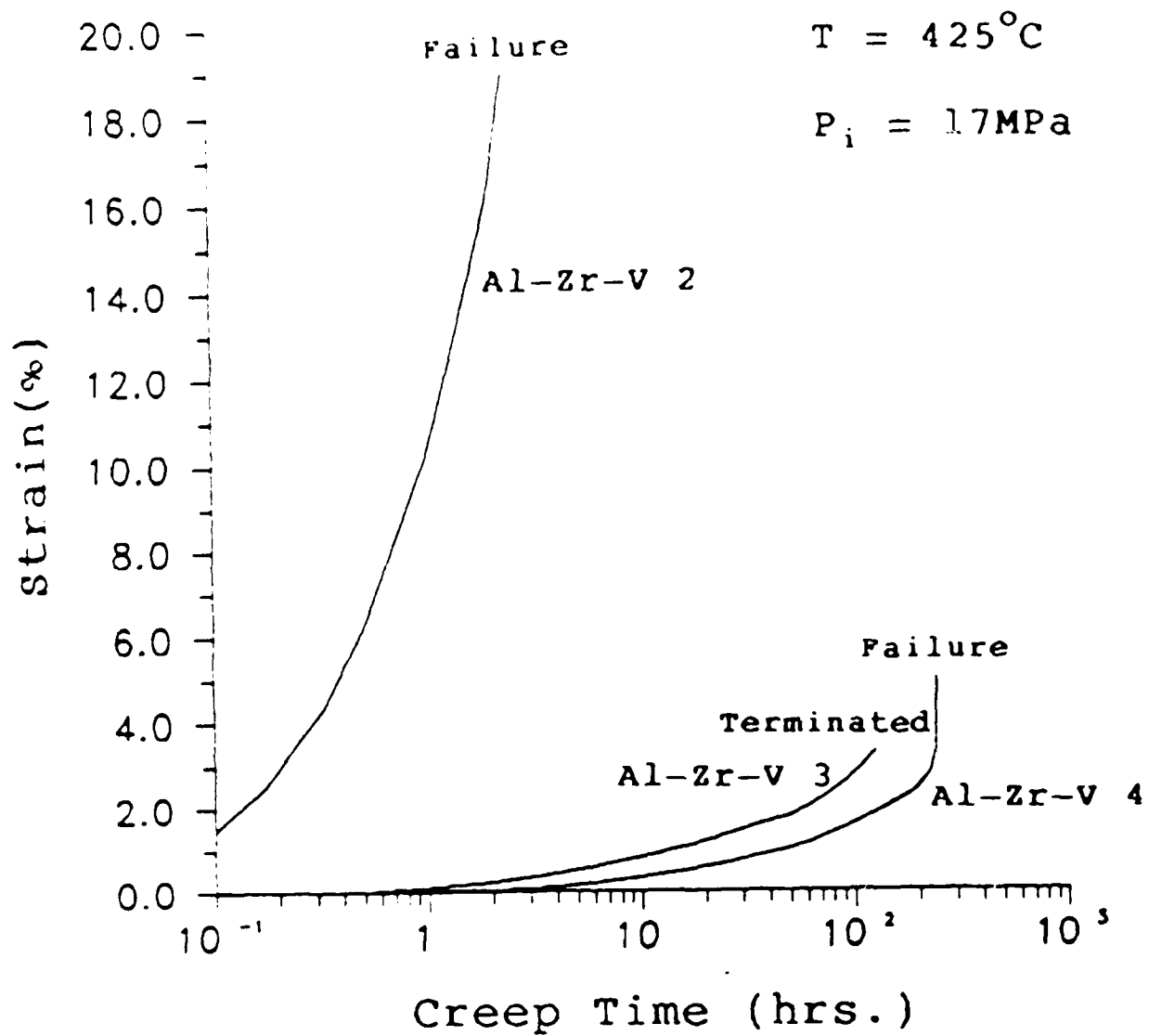


Fig. 7

Creep results of Al-Zr-V alloys at 425°C.

Alloy 2: Al + 5 vol.% Al₃ (Zr_{.75}V_{.25})

Alloy 3: Al + 5 vol.% Al₃ (Zr_{.50}V_{.50})

Alloy 4: Al + 5 vol.% Al₃ (Zr_{.25}V_{.75})

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