Identification of Dispersoids in Al-Mg Alloys Containing Mn

SHENG-LONG LEE and SHINN-TYAN WU

The submicron dispersoids in the ingot of AA 5083 have been identified. They precipitate during the soaking treatment before hot working. Strong evidence suggests that most of them have the composition of $MnAl_4$. A smaller number belong to E phase ($Mg_3Cr_2Al_{18}$) and $CrAl_7$. The presence of the dispersoids of $MnAl_4$ is in contradiction with the ternary phase diagram of Al-Mg-Mn. The particles possess the shape of a rod with a hexagonal cross section. The aspect ratio ranges from one to several tens. These dispersoids may be important to the hot ductility of AA 5000 series alloys.

I. INTRODUCTION

IN a previous publication[1] it has been shown that submicron dispersoids in an alloy of Al-4.85 pct Mg-0.74 pct Mn-0.22 pct Cr were important to the hot ductility of the alloy. The chemical composition had been studied with energy dispersive X-ray spectroscopy (EDS). The major components were either Al or Mg or both. The minor components were mostly Mn, together with small amounts of Fe and Cr. Whether Al or Mg, or both, were major components could not be determined from EDS spectra because the Mg $k\alpha$-peak could not be resolved from the Al $k\alpha$-peak. A preliminary identification using transmission electron microscope (TEM) suggested that the dispersoids had an orthorhombic structure based on $MnAl_6$ with a superlattice whose exact nature needed to be clarified. In the present study, evidence suggesting that the dispersoids belong to the phase of $MnAl_4$[2] has been found. In addition, dispersoids of E phase and $CrAl_7$ have also been found.

It has been known[3] that substructures are formed during hot working through the processes of dynamic recovery and recrystallization. Fracture during hot working can be decisively influenced by dynamic recrystallization.[4-9] Both dynamic processes are strongly affected by the presence of dispersoids.[4,9,10] Consequently, the addition of manganese to aluminum alloys[11] increases the recrystallization temperature, slows down recovery, and hinders grain growth. In AA 5056, grain growth has been shown to be substantially affected by the contents of both Mn and Cr.[12] All these experiences may be related to the interaction between the dispersoids and dislocations, grain boundaries and subboundaries. Therefore, the identification of the dispersoids is of fundamental importance to the science of the hot working of AA 5000 series of alloys.

In the following, the experimental procedure is described and the results of experiments and analysis are discussed in detail before conclusions are drawn.

II. EXPERIMENTAL PROCEDURE

Four different alloys were prepared in a graphite crucible.[1] Emission spectroscopy gave the chemical compositions shown in Table I. Alloy A is a ternary alloy similar to commercial AA 5083 and AA 5456 alloys. The impurities of Fe, Si, and Ti are deliberately excluded to avoid the complications from interdendritic precipitates.[1] Chromium is also excluded because EDS results[1] show it to be a minor alloying element. Alloy B was prepared for investigating the role played by Mg. Alloy C has a composition similar to that of AA 5083 except for the absence of the impurities of Fe, Si, and Ti. It is for studying the dispersoids other than those of $MnAl_4$ in a commercial-like alloy. Alloy D contains impurities like those of commercial alloys.

The first three alloys were given a soaking treatment at 500 °C for twenty-four hours. Alloy D was preheated for one and a half hours at 430 °C and then soaked at 530 °C for eight hours. Afterward the castings were furnace cooled. Specimens for TEM were cut from the castings and thinned with conventional metallographic techniques. The window method,[13] using an electrolyte of 80 pct dehydrated alcohol plus 20 pct perchloric acid, was applied at −40 °C with 15 volts.

A JEOL 200CX scanning transmission electron microscope was used in transmission and diffraction modes, and a double tilting stage was used to obtain the diffraction patterns in various directions. The directions were carefully controlled to simplify the construction of reciprocal lattice from the diffraction patterns. The details are given in the next section.

III. EXPERIMENTAL RESULTS AND ANALYSES

Five of the diffraction patterns of the dispersoids in alloy A are shown in Figure 1. The three-fold symmetry is quite evident in Figure 1(c). The lattice constants obtained from these patterns are $a = 2.86$ nm and $c = 1.25$ nm, to be compared with the known values of $a = 2.841$ nm and $c = 1.238$ nm for $MnAl_4$.[2] These five patterns have covered the Kikuchi map[18] in sufficient detail that the space lattice can be regarded as identified. The lattice constants are sufficiently close to those of $MnAl_4$ to consider the possibility that these dispersoids belong to a variant of $MnAl_4$. Notice that the ratio $c/a = 0.436$ is unusually lower than 1.633 of hcp structure. Therefore the unit cell is compressed along c-axis. Since there are no alloying elements in alloy A other than Mg and Mn, the close similarity between the lattice of $MnAl_4$ and that of the dispersoids strongly suggests that the latter are precipitates of $MnAl_4$ with Mg as a possible minor element. On the other hand, the large differences in atomic radii between Al and Mg and in valence electrons between Mn and Mg, make it highly improbable that Mg may be present in significant concentration in the stoichiometric compound of $MnAl_4$. Therefore it is

SHENG-LONG LEE, Lecturer, and SHINN-TYAN WU, Professor, are with the Department of Materials Science and Engineering, National Tsing-Hua University, Hsinchu, Taiwan, Republic of China.

Table I. Chemical Compositions, Wt Pct

Alloy Designation	Weight Percentage						
	Fe	Si	Mg	Mn	Cr	Ti	Al
A	ND	ND	4.75	0.83	ND	ND	bal
B	ND	ND	ND	1.05	ND	ND	bal
C	ND	ND	4.6	0.62	0.22	ND	bal
D	0.13	0.05	4.84	0.74	0.22	0.066	bal

ND: not detectable by emission spectroscopy
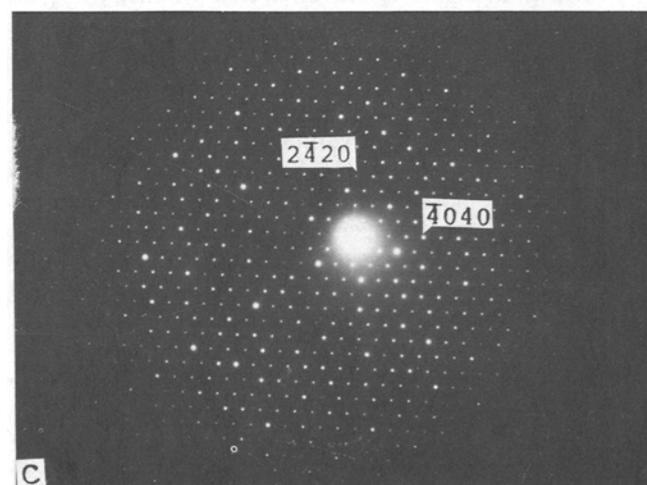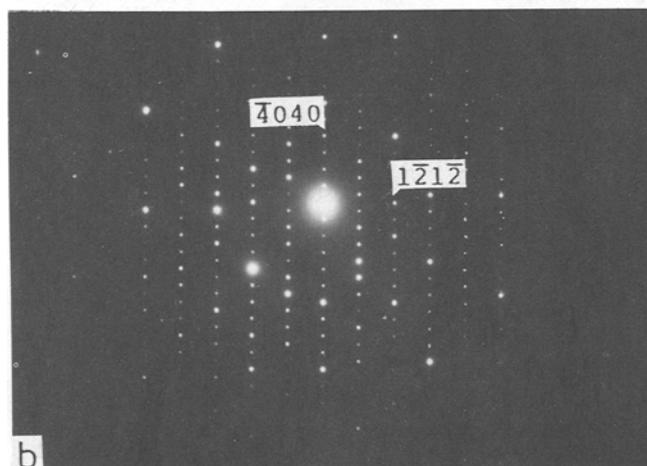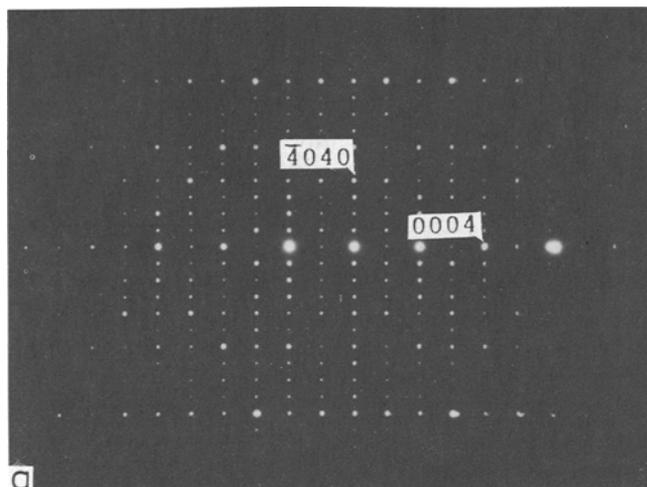
likely that the dispersoids are $MnAl_4$. A more direct confirmation by X-ray diffraction is certainly worthwhile.

In Figure 2, typical micrographs from TEM are shown. From these and numerous others not shown we draw the tentative conclusion that the dispersoids have a rod shape with a hexagonal cross section. The lengthwise direction is along the c-axis. The aspect ratio ranges from one to several tens. The hexagonal cross section is not easily observed because the through-thickness dispersoids in a TEM specimen are easily dislodged from the matrix during electrolytic thinning. The reason is probably that the matrix surrounding the dispersoids is etched at a faster rate so as to be easily perforated. The hexagonal section in Figure 2 was obtained with considerable difficulty.
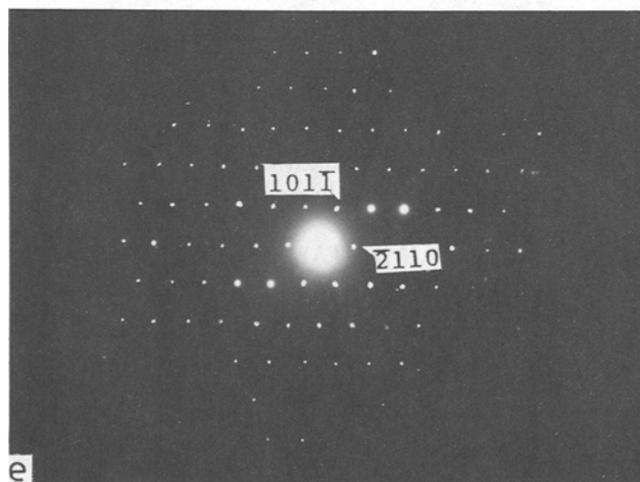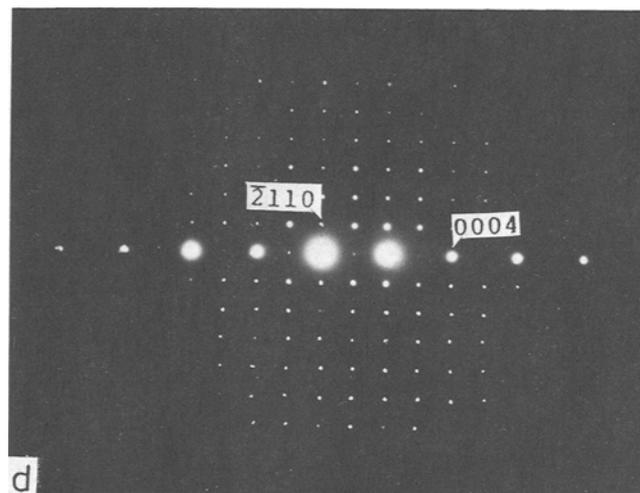
Fig. 1 — SAD patterns of $MnAl_4$ dispersoids with zone axis along (a) [1$\bar{2}$10], (b) [1$\bar{2}$13], (c) [0001], (d) [0$\bar{1}$10], and (e) [0$\bar{1}$11]
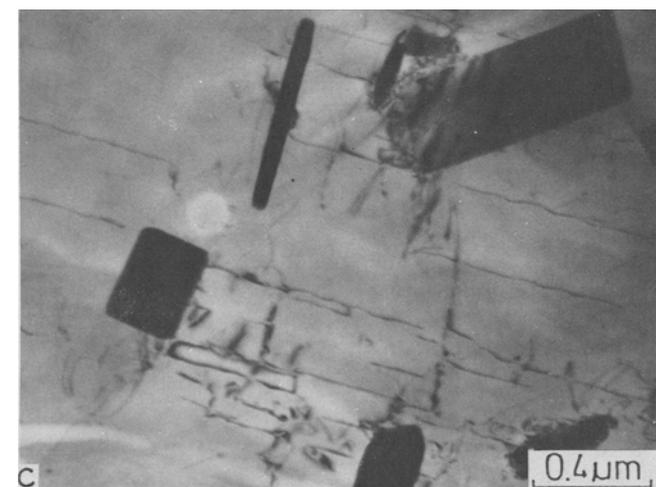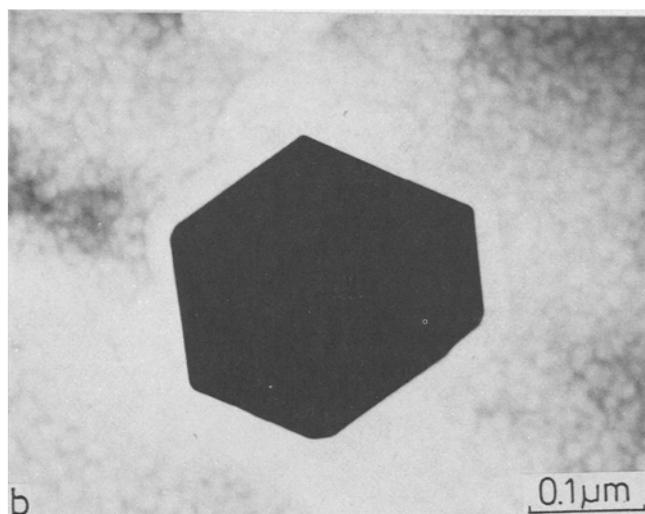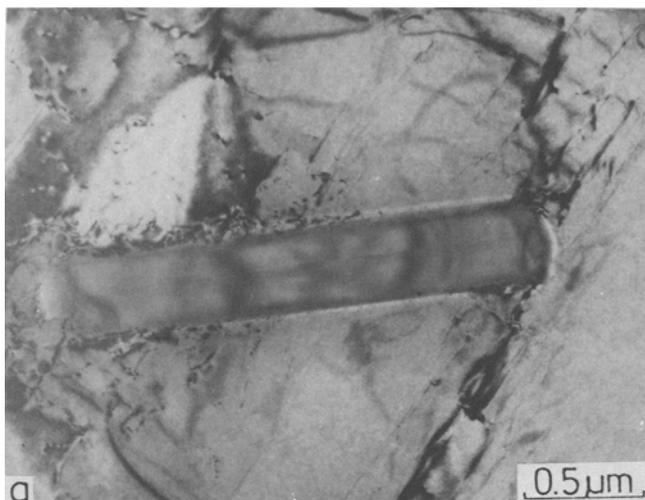
Fig. 2 — The micrographs showing the shape of MnAl₄ dispersoids.

Fig. 3 — An equiaxial particle of $MnAl_6$ at the grain boundary of A alloy.

The result is quite contrary to what is expected from the binary Al-Mn phase diagram[14] which shows that $MnAl_6$ would be expected at 500 °C if magnesium is not present. After extensive searching using selected area diffraction, none of $MnAl_6$ was found within the dendrites. Occasionally equiaxed precipitates of $MnAl_6$ were found on the grain boundaries. An example is shown in Figure 3. There-

fore $MnAl_4$ seems to be thermodynamically more stable than $MnAl_6$.

To confirm our finding, alloy B was prepared with the composition of Al-1.05 pct Mn. Mg had been deliberately excluded. The soaking treatment did result in the precipitation of $MnAl_6$ as shown in Figure 4, as predicted by the binary phase diagram. Both inter- and intradendritic precipitates are observed. $MnAl_4$ phase is absent. Therefore 4.75 pct of Mg in alloy A renders $MnAl_4$ more stable than $MnAl_6$ at 500 °C. Apparently magnesium and manganese interact so strongly that the chemical potential of Mn in the ternary solid solution increases substantially. The Al-rich corner of the ternary phase diagram needs to be reconsidered.[15,16,17]

Alloy C contains 0.22 pct of chromium. Its composition is almost identical to commercial AA 5083 alloy. Most of the dispersoids present after the soaking treatment belonged to $MnAl_4$ as indicated by the particle shape. Occasionally $MnAl_6$ particles were found on the grain boundary, but not within the grain, as shown in Figure 5. Dispersoids of E phase ($Mg_3Cr_2Al_{18}$) and $CrAl_7$[2] could also be found within the dendrites as shown in Figures 6 and 7. The morphology is clearly different from that of $MnAl_4$, allowing the particles to be easily distinguished. Their numbers increase with chromium content, yet are smaller than the dispersoids of $MnAl_4$.

To investigate the possible influence of Fe and Si impurities on the precipitation of the dispersoids, alloy D was prepared. The soaking time has been shortened to simulate industrial practices. The dispersoid morphology and the diffraction patterns are shown in Figure 8. A comparison with Figure 1 indicates that the dispersoids in alloys A and D are identical. Therefore Fe and Si do not have major influences on the precipitation of the dispersoids. The precipitation of $MnAl_6$ in alloy B is in accord with the binary phase diagram. This implies that the soaking treatment of alloys A, B, and C is enough to achieve thermal equilibrium. Therefore, $MnAl_4$ in alloys A and C is an equilibrium phase. The fact that the same phase is also found in alloy D seems to imply that Fe up to 0.13 pct and Si up to 0.05 pct do not alter significantly the kinetics and thermodynamics of the precipitation. Previous work,[4,9,19-21] in which the identity of
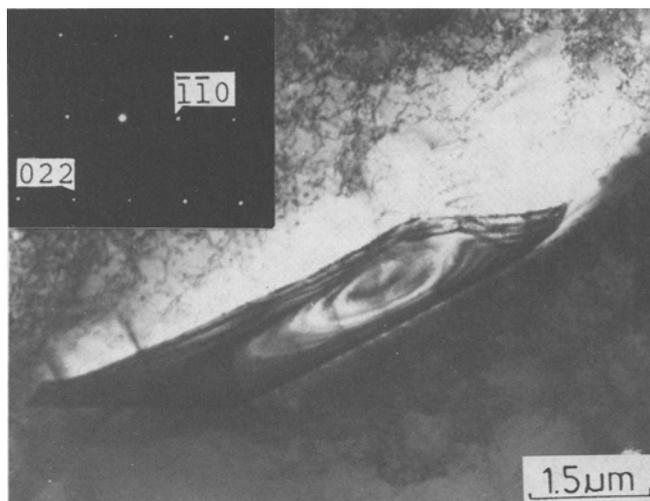
(a)
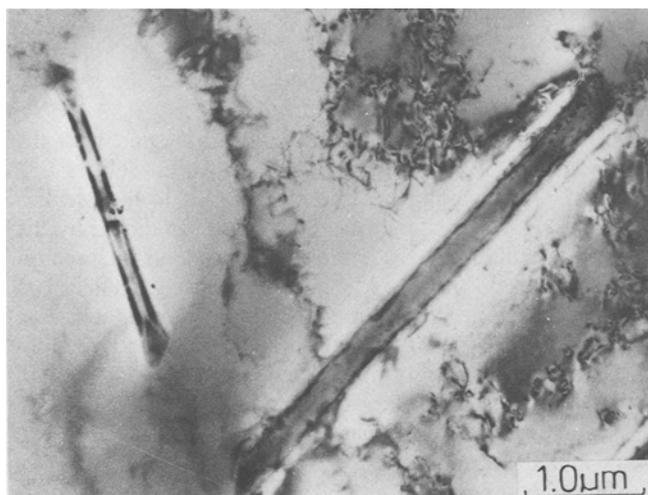
(b)

Fig. 4 — (a) MnAl₆ particle of B alloy at the grain boundary together with the diffraction pattern of [1̄1̄1] zone axis. (b) Flat needle-shape MnAl₆ precipitates of B alloy within the intradendritic region.
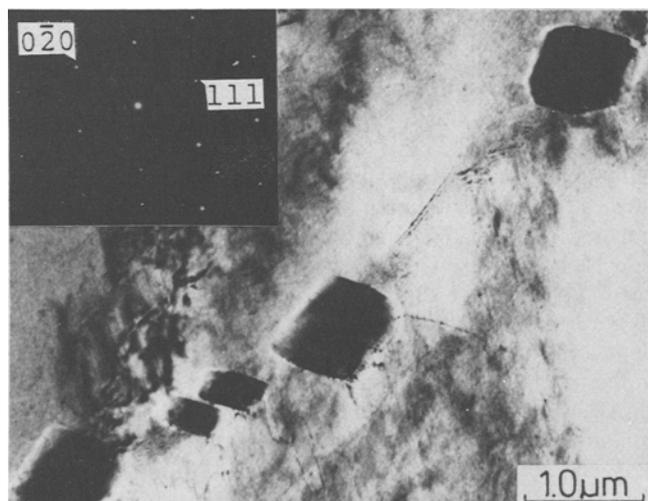
Fig 5 — MnAl₆ particles of C alloy at the grain boundary together with the diffraction pattern of [101̄] zone axis.
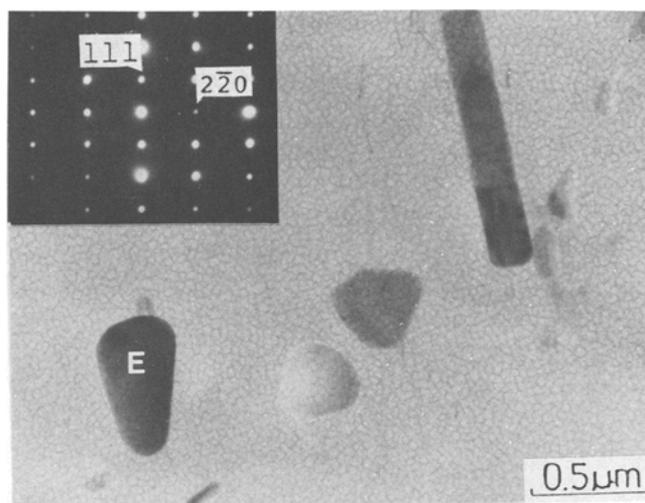
Fig. 6 — The dispersoids of E phase and MnAl₄ phase in C alloy together with the diffraction pattern of E phase with a [11̄2̄] zone axis.
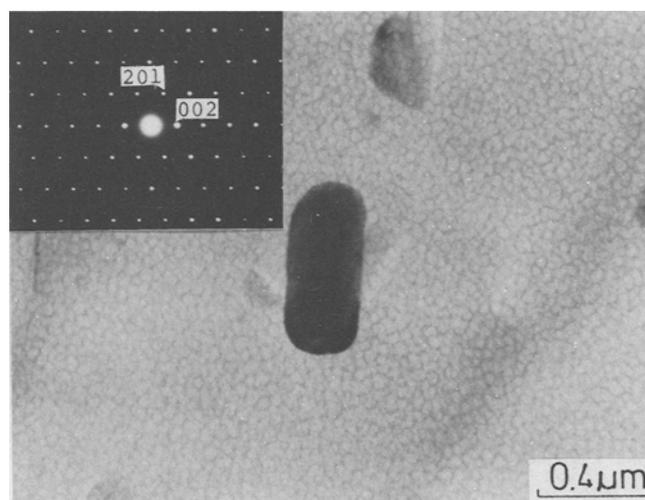
Fig 7 — CrAl₇ phase at intradendritic region together with the diffraction pattern of [010] zone axis.

the dispersoids is mentioned, have not provided any crystallographic data. Ours is the first one as far as we are aware of. Since alloy D is similar to AA 5083 in chemical composition and soaking treatment, it is reasonable to suggest that the dispersoids of MnAl₄ may be important to the hot ductility of AA 5083.[1]

IV. CONCLUSIONS

The dispersoids in AA 5083 alloy which are important to the hot ductility have been identified by selected area diffraction of TEM. They have the same hexagonal lattice of MnAl₄. Therefore the dispersoids are precipitates of MnAl₄ containing minor components of Fe and Cr.[1] Their presence at 500 °C is in contradiction with the current ternary phase diagram of Al-Mg-Mn.[15,16,17] The dispersoids have a rod shape with a hexagonal cross section. The lengthwise direc-
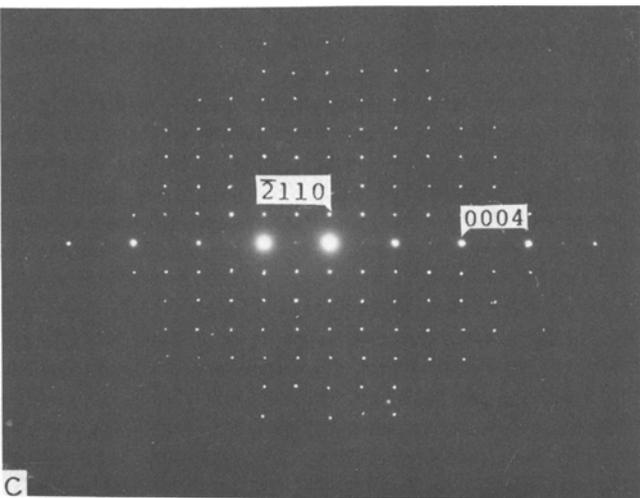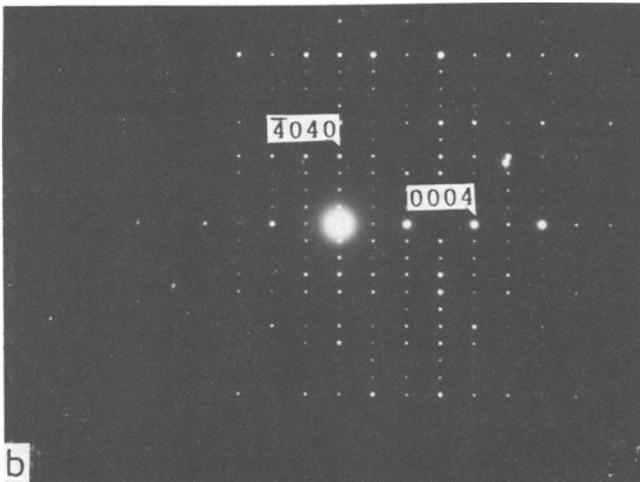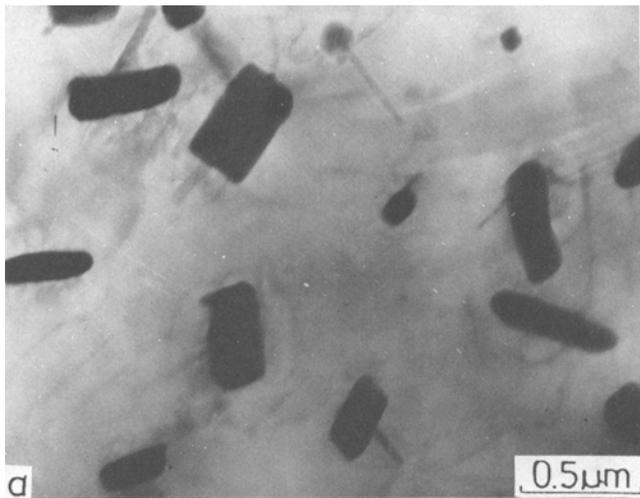
Fig. 8—The micrographs showing (a) the morphology and SAD patterns along (b) [1210] and (c) [0110] of the dispersoids in alloy D which contain Fe and Si impurities

tion is along the c-axis. The aspect ratio ranges from one to several tens. In addition to the precipitates of $MnAl_4$, some of the dispersoids containing chromium have also been identified. They are precipitates of $CrAl_7$ and $Mg_3Cr_2Al_{18}$ (E phase).[2] Some particles of $MnAl_6$ have been found in the interdendritic regions.

ACKNOWLEDGMENTS

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