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AN ELECTRON MICROSCOPY STUDY OF THE SOLUTION TREATMENT OF MAR 350 AND MAR 400 MARAGING STEELS

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ABSTRACT

A study of the effect of solution treatment on the microstructure of types AR 350 and MAR 400 maraging steels has been carried out using transmission lectron microscopy (TEM). The aim of the study was to determine the heat reatments needed to produce fine-grained, single-phase microstructures which, fter ageing at 500°C, were likely to have acceptable combinations of strength, ughness and ductility. The main results are a series of fold out montages ich present a detailed description of the microstructure.

Results for MAR 350 confirm that a fine-grained microstructure can be oduced by cold working followed by the optimum solution treatment for this eel which is 60 minutes at 820°C; higher solution temperatures result in pid grain growth.

Continued.

For MAR 400, a minimum solution temperature of 1000°C is needed to ensure a single-phase microstructure. However, at this temperature, grain growth occurs quickly and times at temperature of about 15 minutes are the maximum allowable if a fine-grained microstructure is to be retained. Samples heat treated between 900 and 1000°C contain a second phase which was identified as the μ-phase $(FeCo)_7Mo_6$. Below 900°C there is a third, metastable, phase which was not identified. Measurement of grain size as a function of temperature indicates that the μ-phase has an inhibiting role in the recrystallisation process.

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ELECTRON MICROSCOPY; GRAIN SIZE; MARAGING STEELS; DUCTILITY; FRACTURE PROPERTIES; GRAIN REFINEMENT; RECRYSTALLIZATION; METALLOGRAPHY; HEAT TREATMENTS

CONTENTS

CONTENTS (Continued)

1. INTRODUCTION

As a result of the interest in the feasibility of enriching uranium by means of the gas centrifuge process, a study of potential materials of construction has been undertaken. The physical attributes required of these materials are high strength-to-weight ratio; adequate ductility; and low cost compared to carbon fibre composites. Maraging steels were selected as candidate materials since they may be easily formed in the solution-treated condition before the development of high strength by low temperature ageing. Although maraging steels are not stainless and hence susceptible to stress corrosion and hydrogen embrittlement (Dautovich & Floreen 1973), they compare favourably with other non-stainless, high-strength steels.

Before ageing, normally carried out at ~ 490°C, maraging steels are solution-treated at temperatures greater than 800°C. After air cooling from the solution temperature, a martensitic structure is formed, which is easily shaped because of its low carbon content. Solution treatment ensures that all precipitates are in solution and that grain growth is kept to a minimum. These two conditions are needed to obtain an acceptable combination of strength, toughness and ductility. The presence of precipitates leads to poor toughness, whereas an increasing grain size is accompanied by decreasing ductility; hence, there is a need to know the optimum solution treatment.

The solution temperature depends on the alloy composition. With grades of maraging steel up to MAR 350*, a temperature of about 820°C is generally recommended (Rack & Kalish 1971). However, since MAR 400 steels contain larger Co and Mo contents, higher temperatures are required to ensure the complete solution of precipitates. The optimum solution treatment for MAR 400 is the subject of dispute and several heat treatments, some of which involve high temperature working, are given in the literature (Magnée et al. 1973, Nakazawa et al. 1978). Also, the possible formation of precipitates during heating and cooling has been reported (Tarantova et al. 1970, Kawabe et al. 1978). In the case of MAR 400, a number of precipitates have been identified in samples subjected to low-temperature solution treatment (Drapier et al. 1971). However, there is considerable overlap of the lattice d-spacings measured from these precipitates and their correct identification is doubtful.

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* 350 denotes the ultimate tensile strength of the steel in KSI ($lb\ in^{-2} \times 10^3$) units, and has gained wide acceptance in practice. Since this paper is not concerned with numerical mechanical properties, the designations MAR 350 and MAR 400 will be used.

The aim of this investigation was to study the effect of various solution treatments on the microstructure of MAR 350 and MAR 400 steels by transmission electron microscopy (TEM). It was hoped to find minimum temperatures for the recrystallisation and complete solution of precipitates as a prelude to establishing the heat treatment needed to produce a microstructure compatible with optimum mechanical properties.

2. EXPERIMENTAL

Table 1 lists the chemical compositions of MAR 350 and MAR 400 maraging steels. Before heat treatment, a 17 mm diameter rod of MAR 350 was reduced to a 0.25 mm thick strip by cold rolling. Details of the various heat treatments of the MAR 350 samples are listed in Table 2. A MAR 400 rod of the same diameter was similarly reduced by cold rolling but it required annealing for 1 hour at 1150°C before the final 50 per cent reduction. Details of subsequent heat treatments of MAR 400 samples are listed in Table 3.

2.1 Optical Metallography

Mechanically ground samples were electrolytically polished and etched. Polishing was carried out at 60-70 V using a 9 per cent perchloric acid in glacial acetic solution at room temperature. Etching was also carried out at room temperature using a solution of 1 per cent hydrochloric acid in methylated spirits at 1-7 V.

2.2 Transmission Electron Microscopy

After heat treatment, the 0.25 mm thick strip samples were chemically reduced to a thickness of 0.008 mm using a solution of 5 per cent hydrofluoric acid in hydrogen peroxide. Three millimetre diameter discs punched from this thinned material were electropolished in a Struers Tenupol electropolisher using a solution of 6 per cent perchloric acid, 60 per cent methanol, 34 per cent Butycellusolve at -30°C, a speed setting of 1 and a voltage of 47 V. Transmission electron microscopy was carried out in a JEM 7A equipped with a specially designed beam deflection unit.

3. RESULTS

The major results of this investigation are in the form of TEM montages. Figures 1 to 24 are a series of fold-out montages, typical of the microstructures observed in the MAR 350 and MAR 400 samples in the cold-worked and heat-treated condition. Each fold-out is supplemented by an optical micrograph and, in the case of the MAR 400 samples, a histogram of the size distribution of any precipitates observed in the electron micrograph. In addition, each fold-out is accompanied by a brief summary of the following characteristics: (a) degree of recrystallisation; (b) estimate of the

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$$V_v = \sum_i (Vv)_i$$

$$= \sum_i \frac{M^2}{A} \times \frac{\pi}{6} (D_i)^3 \times \frac{N_i}{(t + D_i)}$$

where $(Vv)_i$ = volume fraction in class i,

M = micrograph magnification,

A = area considered,

D_i = average particle diameter in class i,

N_i = number of particles in class i observed, and

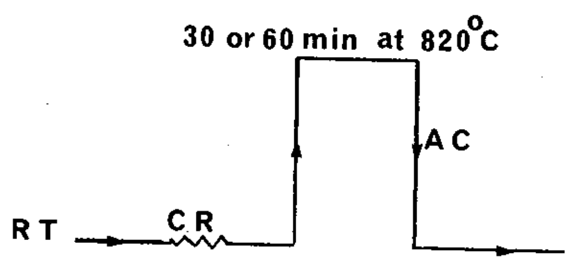
t = foil thickness = 0.15 nm.

The effect of heat treatment on the initial cold-worked structure of the AR 350 and MAR 400 steels will be briefly described. Sub-section headings riefly describe the type of thermo-mechanical treatment received by the ample before metallographic examination. These headings are used as figure aptions where appropriate.

3.1 MAR 350

Figure 1 shows the microstructure of the MAR 350 steel samples before they ere submitted to heat treatment (Table 2). Inclusions (or precipitates) of arious sizes ranging from 0.1 to 1 µm diameter may be observed in the heavily old-worked structure. Inclusions were noted in most of the heat-treated AR 350 samples. Since number and distribution of these inclusions were nall, and of little significance, a size analysis was not carried out.

(a) Solution treatment at 820°C



AC = Air cooling

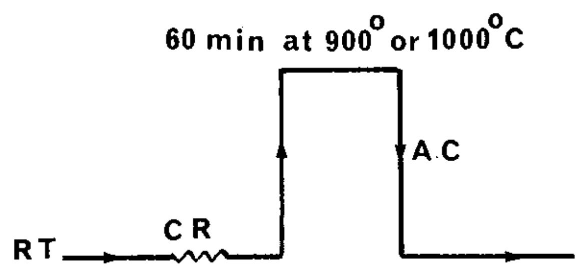
RT = Room temperature

CR = Cold rolling

After 30 minutes at 820°C, some recrystallisation had taken place (Figure 2). After 60 minutes at 820°C, recrystallisation was complete with a small grain size of ~ 25 μm (Figure 3).

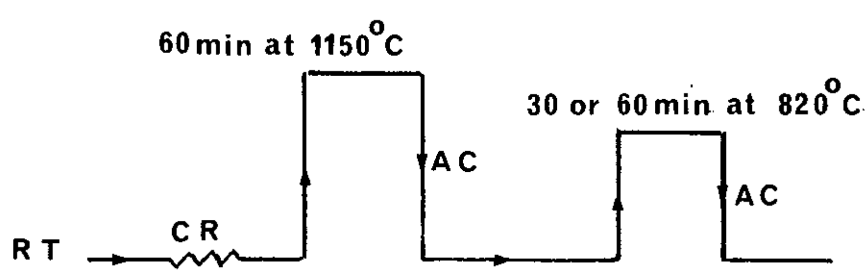
Small and large inclusions remained after 30 minutes at 820°C. However, after 60 minutes at 820°C, most of the small particles had dissolved leaving a random distribution of large particles. The dissolution of the smaller particles suggests that they were precipitates formed when the original 16 mm diameter rod was cooled from its shaping temperature. It was thought that the large remaining particles were most likely to be carbides and nitrides of titanium. Analysis of large particles in a scanning electron microscope (SEM) using an energy dispersive X-ray analyser confirmed that they contained titanium. Holes in the TEM foil where large particles have fallen out may be seen in Figure 3.

(b) Solution treatment at 900°C and 1000°C



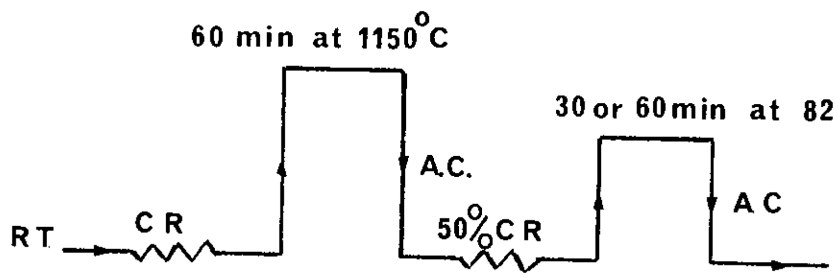
Cold-worked samples were heat treated for 60 minutes at 900 and 1000°C (Figures 4 and 5), and produced well recrystallised structures. A few isolated inclusions were observed in each sample. As a result of grain growth, the grain sizes after heat treatment at 900 and 1000°C were approximately 60 μm and 125 μm, respectively.

(c) Solution treatment at 1150°C followed by heat treatment at 820°C



Samples which had undergone solution treatment at 1150°C followed by air
ooling were heat treated at 820°C for 30 and 60 minutes (Figures 6 and 7).
very large grain size of ~ 250 μm resulting from the 1150°C treatment was
oserved in both samples. Grain refinement did not occur with heat treatment
: 820°C, despite the strain introduced by the martensitic transformation
ccurring during air cooling from 1150°C. Very few inclusions were observed
1 these samples.

(d) Solution treatment at 1150°C followed by cold rolling and heat treatment at 820°C



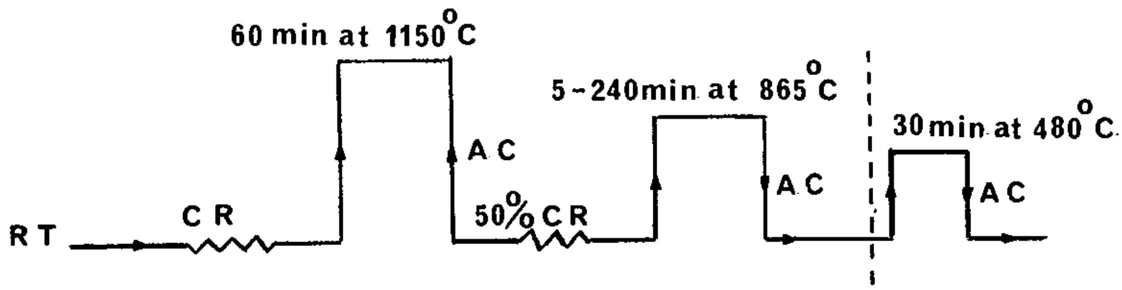
Samples which had been solution treated at 1150°C for 60 minutes, were
ld reduced by 50 per cent before heat treating at 820°C for 30 and 60 minutes
igures 8 and 9). Recrystallisation occurred in both samples with small grain
zes of ~ 15 μm after 30 minutes and 25 μm after 60 minutes. Compared with the
mples which had not been cold reduced (Section 3.1 (c), Figures 6 and 7),
ere was significant grain refinement. A few discrete holes were observed in
e TEM foil; usually, this is taken to mean that an included particle has
opped out.

No particles were observed in the samples which had been similarly heat
eated but had not undergone cold rolling (Section 3.1 (c), Figures 6 and 7).
erefore, it is possible that they were the result of contamination from the
lls, although precautions to produce 'clean' surfaces were taken. It is also
ssible that TiN and TiC precipitates remained undissolved after this solution
eatment at 1150°C.

3.2 MAR 400

Figure 10 shows the microstructure of the MAR 400 steel before undergoing
e treatments listed in Table 3. The cold-worked structure is relatively
e from inclusions or precipitates. The elongated grain size is about 200 μm.

(a) Solution treatment at 1150°C followed by cold rolling and heat treatment at 865°C



Heat treatment times at 860°C ranged between 5 and 240 minutes. Two samples were aged for 30 minutes at 480°C after treatment at 865°C. Since this ageing process would not affect the solution-treated microstructure, these samples may be considered as part of the series.

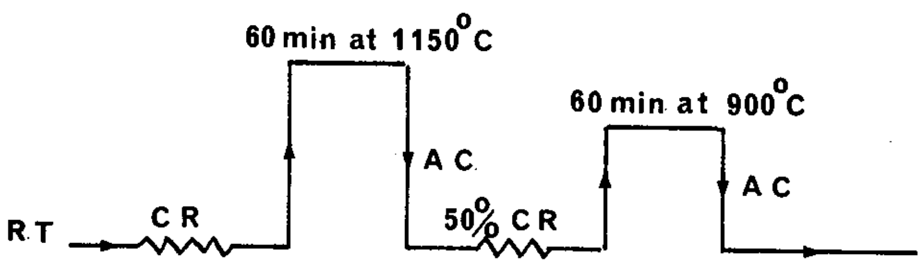
The optical micrographs show complex structures which have retained the rolling or deformation texture. Close examination reveals the presence of small particles dispersed throughout the samples but there is no evidence of recrystallisation. The TE micrographs provide considerable detail of microstructure. The absence of recrystallisation is confirmed, some evidence of deformation is noted and, more importantly, precipitates are observed in all samples.

In samples heat treated for 5 and 15 minutes (Figures 11 and 12), precipitates having two distinct morphologies are noted. Larger particles have been labelled type A and correspond to the particles observed in the optical micrographs. Small particles, usually < 0.05 µm diameter, are more rounded, more numerous and have been labelled type B. Attempts to identify these precipitates were made on the same samples, using electron diffraction and energy dispersive X-ray analysis. (Details of the diffraction patterns and analysis are given in Appendix A.) The type A precipitate may be unequivocally identified as the intermetallic µ-phase, having the composition $(FeCo)_7Mo_6$. Owing to the small particle size, identification of the type B phase has proved more difficult. The diffraction lattice spacings for this phase show considerable overlap with the lines from the µ-phase. The non-overlapping lines do not allow the precipitate to be defined as either the σ-phase FeMo or Fe_2Mo, the latter being an equilibrium phase in the Fe-Mo diagram below 900°C (Sinha et al. 1967). Using specially heat-treated samples, work is continuing in an attempt to identify unambiguously this type B phase.

The histograms of precipitate size distribution are shown in Figure 25. ne rapid disappearance of the type B particles having average diameters 0.05 μm with increasing time is clearly shown. Particles having average ameters < 0.025 μm were only noted in samples heat treated for 5 and 15 nutes. The rapid growth in particle size is confirmed by examining the plot f mean particle diameter versus time at 865°C (Figure 26(a)). Close nspection of samples treated for longer than 30 minutes suggests an absence f particles having the type B morphology. It may be concluded that the nidentified type B precipitate either forms rapidly during heating through s stable temperature range or is a metastable phase at 865°C.

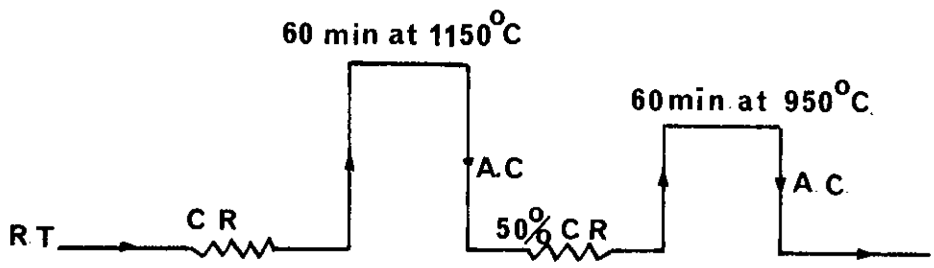
The μ phase (labelled type A) is stable at 865°C. The size histograms ow a steady increase in particle size with a constant volume of phase. he exact volume measurements must be treated with caution owing to the nall sample area.) In the large particles, which extend up to 0.65 μm, idence of internal faulting may be observed, particularly in samples heat eated for longer times. The essentially constant 2.5% precipitate volume asured may be compared with the ~ 14% theoretically possible if all of the per cent Mo present in the alloy precipitated in the form of $(FeCo)_7Mo_6$.

(b) Solution treatment at 1150°C followed by cold rolling and heat treatment at 900°C



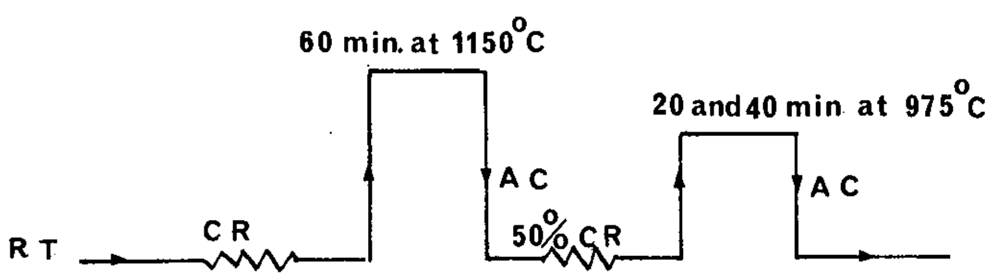
One sample was treated for 60 minutes at 900°C (Figure 17). Some evidence r partial recrystallisation can be seen in the optical and TE micrographs. en this is compared with the heat treatment at 865°C for 60 minutes, there is shift to larger size ranges of the μ-phase particles, labelled A in the size stribution histograms (Figure 25). Also, as can be seen in Figure 26(b), a ry small decrease in mean particle diameter is noted. There is no evidence particles having the phase B morphology. The total precipitate volume 2%) is similar to that measured after 45 minutes at 865°C.

(c) Solution treatment at 1150°C followed by cold rolling and heat treatment at 950°C



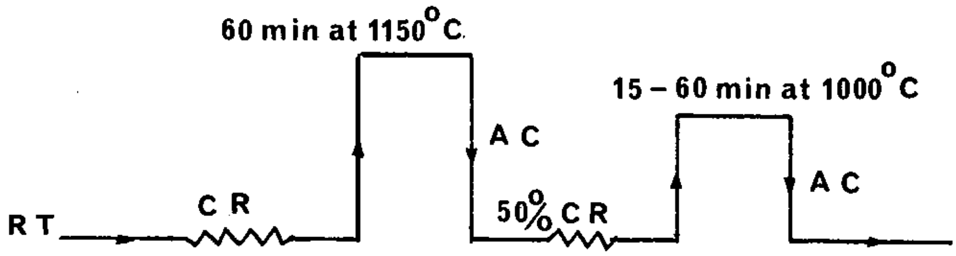
Some signs of recrystallisation are present in the optical micrograph of a sample treated for 60 minutes at 950°C (Figure 18). Examination of the TE micrographs confirms the occurrence of recrystallisation and that the prior austenite (γ) grain size is ~ 15 μm. Despite the recrystallisation, a significant quantity of μ phase (~ 1%) remains undissolved. Particles of μ phase having sizes up to 0.64 μm in diameter are observed, although the mean particle diameter has reduced considerably compared with that measured after 60 minutes at 900°C (see Figure 26 (b)).

(d) Solution treatment at 1150°C followed by cold rolling and heat treatment at 975°C



After 20 minutes at 975°C, recrystallisation occurred with a prior γ grain size of ~ 25 μm (Figure 19). A small amount (~ 0.5 vol.%) of μ phase can still be observed in the sample. After 40 minutes at 975°C, the grain size had not increased significantly and a similar quantity of μ phase was still detected (Figure 20). This level of μ phase would have a deleterious effect on fracture toughness.

(e) Solution treatment at 1150°C followed by cold rolling and heat treatment at 1000°C



After 15 minutes at 1000°C (Figure 21) complete recrystallisation had taken place and all precipitates were in solution. By increasing the time at 1000°C to 60 minutes, the prior austenite γ grain size increased from ~ 35 μm to ~ 125 μm (Figures 22-24). In the sample heat treated for 15 minutes there was still some evidence of the rolling direction.

4. OPTIMUM SOLUTION TREATMENTS

The twin aims of the maraging steel solution treatment are a fine-grained and single-phase microstructure. These goals must be achieved to ensure an acceptable combination of strength, toughness and ductility following a low temperature ageing step.

Plots of the logarithm of grain size versus solution temperature for the maraging samples studied are presented in Figure 27. The data points include a soaking time of 60 minutes at the required temperature, except in the case of the MAR 400 sample treated at 975°C when the soaking time was 40 minutes. Inserted into Figure 27 is a plot of the logarithm of grain size for MAR 400 as a function of time at 1000°C.

The data presented for MAR 350 in Figure 27 are similar to those previously reported (Rack 1978). A fine-grained, single-phase microstructure was obtained after 60 minutes at 820°C. A gradual increase in grain size accompanied increasing solution temperature. These recrystallisation characteristics make it relatively easy to produce satisfactory microstructures.

The recrystallisation and grain-growth behaviour of MAR 400 contrasts with that observed in MAR 350. Recrystallisation of MAR 400 did not occur at 865°C. The absence of recrystallisation could not be anticipated on the basis of steel composition and associated austenite reversion temperatures, A_f. Published data (Rack & Kalish 1971, Nakazawa et al. 1978) indicate that the A_f temperature for MAR 400 is only ~ 30°C higher than the A_f temperature for MAR 350.

Recrystallisation occurred in MAR 400 above 900°C together with a large rate of change of grain size with temperature. This behaviour points to the inhibiting role of the μ-phase in the recrystallisation process. At 865°C, the μ-phase occupies approximately 2.5 vol.% and recrystallisation does not take place. At 900°C, the volume of μ-phase is essentially unchanged and some signs of recrystallisation are noted. Above 900°C, the μ-phase progressively dissolved, as reflected in the mean particle diameter versus temperature plot in Figure 26(b), and more than an order of magnitude increase in grain size accompanied an increase in solution temperature from 950 to 1000°C. At 1000°C and higher, the μ-phase is no longer observed in the structure. The rate of increase of grain size fell and, within the error of determination, was similar to that noted with MAR 350.

In addition, all MAR 400 samples solution treated below 1000°C were two-phase, even after recrystallisation. Thus, samples heat treated at 950-975°C to produce a fine grained microstructure, likely to exhibit good ductility, were unacceptable, since the presence of μ-phase particles would ensure poor toughness. Hence, the minimum acceptable solution temperature for MAR 400 steels is 1000°C. At this temperature, conversion of the μ-phase to solution occurred after only 15 minutes, and a very satisfactory grain size of ~ 35 μm was measured. However, as the insert in Figure 27 demonstrates, after only 30 minutes at 1000°C, the grain size had doubled and could cause a significant fall in ductility [Nakazawa et al. 1978].

Clearly, if an acceptable fine-grained MAR 400 microstructure free of precipitates is to be produced by heat treatment alone, short duration, well controlled treatment at 1000°C is required. This would not be a major problem with thin plate or sheet materials; however, solution treatment of components having relatively complex cross sections would be difficult.

5. CONCLUSIONS

5.1 MAR 350

(a) Fine-grained, single-phase microstructures were obtained after 60 minutes at 820°C. TiC and TiN inclusions present in the as-received material were undissolved after this treatment.

(b) After solution treatment at 1150°C for 60 minutes, TiC and TiN particles were still present. Also, very coarse-grained microstructures resulted from this treatment. Grain refinement did not occur after heat treatment at 820°C unless preceded by cold working. The latter procedures produced a fine-grained microstructure.

5.2 MAR 400

(a) Solution treatment at 1000°C produced a recrystallised, single-phase MAR 400 microstructure. At this temperature, grain growth with time was rapid and less than 30 minutes at temperature was required to retain a fine-grained structure.

(b) Although recrystallisation occurred above 900°C, samples heat treated below 1000°C were not single phase.

(c) Above 900°C the precipitate was identified as a μ-phase having the composition $(FeCo)_7Mo_6$.

(d) Samples heat treated at 865°C contained μ-phase and, for treatment times less than 60 minutes, another small, widely dispersed metastable precipitate which was not identified.

(e) A study of grain size as a function of temperature points to the inhibiting role of the μ-phase in the recrystallisation process. At temperatures above 900°C, where the μ-phase dissolved gradually, extremely rapid grain growth was measured.

6. ACKNOWLEDGEMENTS

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TABLE 1

COMPOSITIONS OF MARAGING STEELS (wt.%)

Element	Sandvik 350		Sandvik 400	
	Spec.	Analysis	Spec.	Analysis
C	0.006	0.010	0.004	0.010
Si	0.04	0.04	0.02	0.04
Mn	0.04	0.03	0.05	0.01
P	0.007	0.004	0.006	0.003
S	0.010	0.007	0.008	0.006
Ni	18.9	18.15	12.2	13.20
Cr	0.09	<0.01	0.030	<0.01
Mo	4.50	4.40	10.1	9.45
Ti	1.64	1.46	na	0.13
Al	0.13	0.17	0.002	0.005
Co	11.9	10.8	15.0	13.1
Nb	na	<0.01	na	<0.01
B	na	0.004	na	0.002
Cu	na	0.01	na	0.01
Zr	na	na	na	na
V	na	0.01	na	0.01
Fe	balance	balance	balance	balance
N	0.002	0.0020	0.007	0.0025

na not analysed

TABLE 2

SANDVIK MAR 350 TREATMENTS

Initial Heat Treatment		Mechanical Deformation	Solution Treatment	
Temp. (°C)	Time (min)		Temp. (°C)	Time (min)
-	-	-	820	30
-	-	-	820	60
-	-	-	900	60
-	-	-	1000	60
1150	30	-	820	30
	60	-	820	60
	30	CR 50%	820	30
	60	CR 50%	820	60

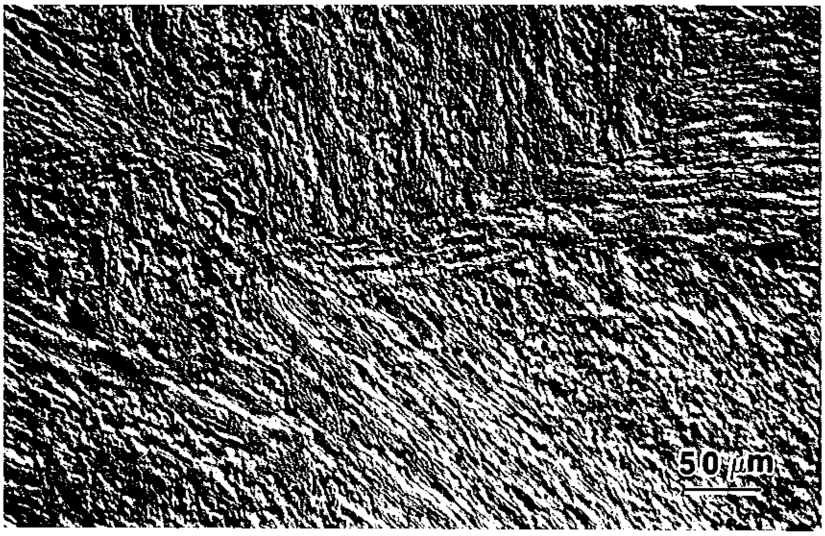
All samples were heavily cold rolled (CR) before receiving heat treatment

TABLE 3

SANDVIK MAR 400 TREATMENTS

Solution Treatment		Ageing Treatment	
Temp. (°C)	Time (min)	Temp. (°C)	Time (min)
865	5	-	-
	15	-	-
	30	-	-
	60	-	-
	120	480	30
	240	480	30
900	60	-	-
950	60	-	-
975	20	-	-
	40	-	-
1000	15	-	-
	30	-	-
	45	-	-
	60	-	-

All samples were solution treated for 1 hour at 1150°C and 50% cold reduced before receiving the heat treatments shown.



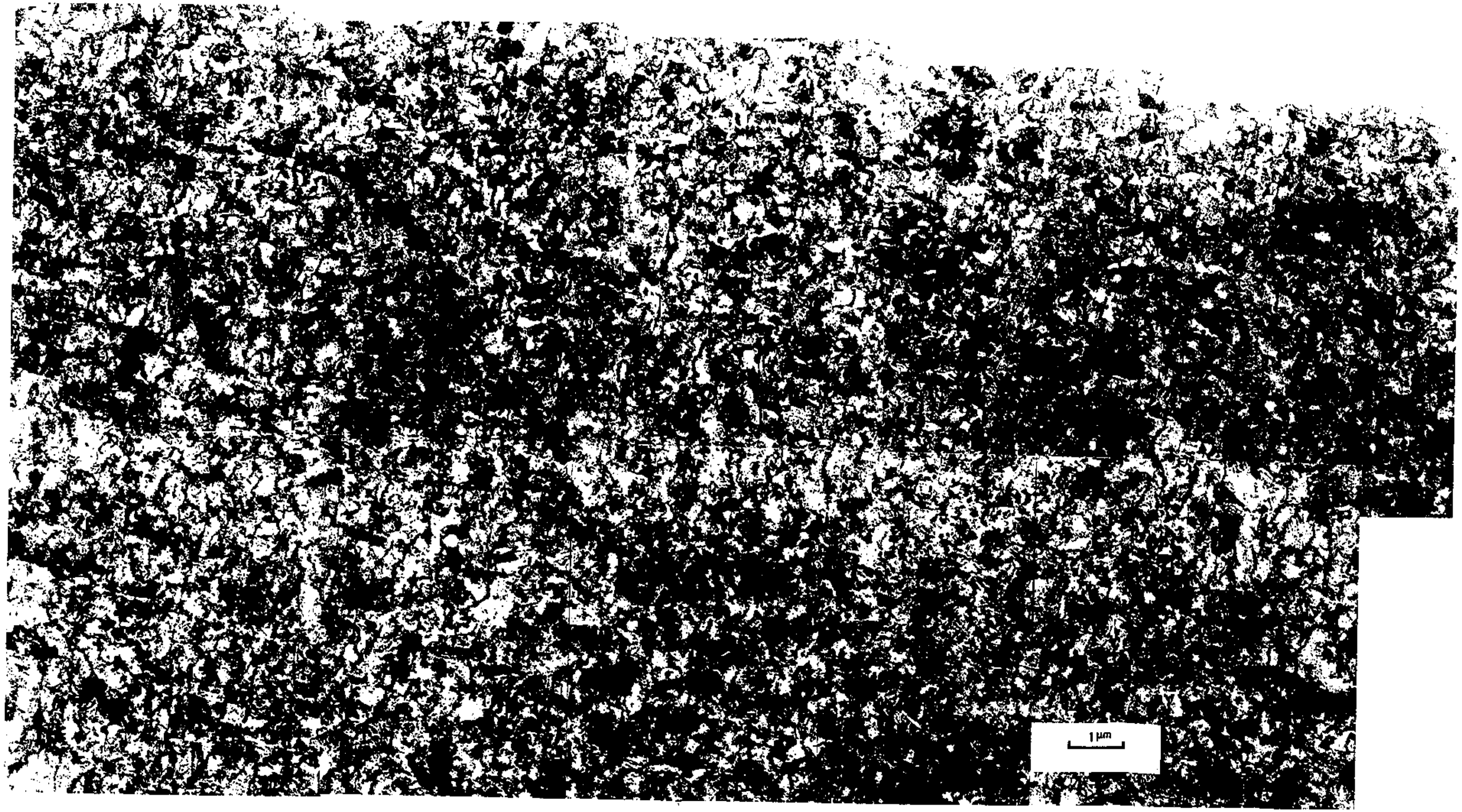
OBSERVATIONS

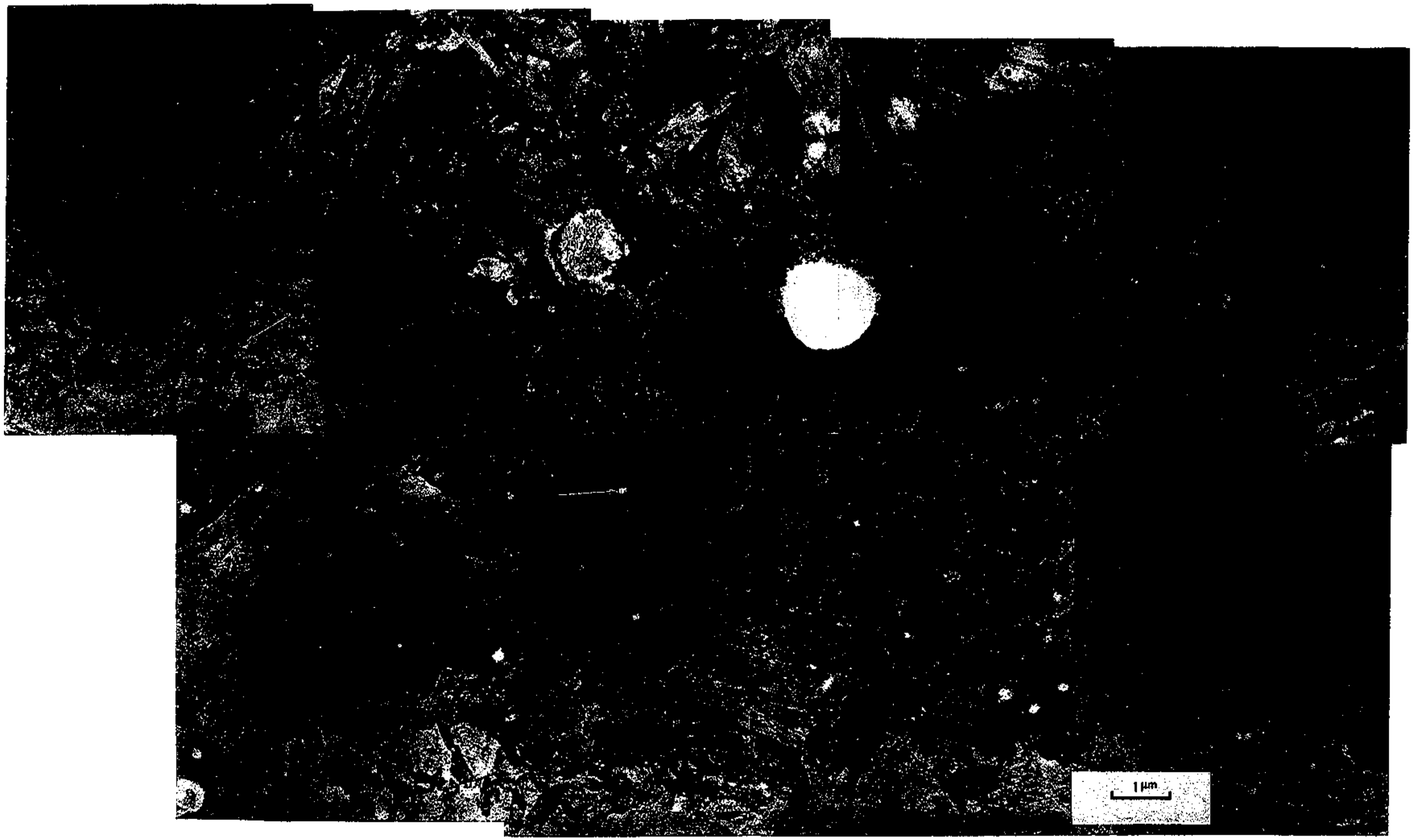
(i) Heavily cold worked structure.

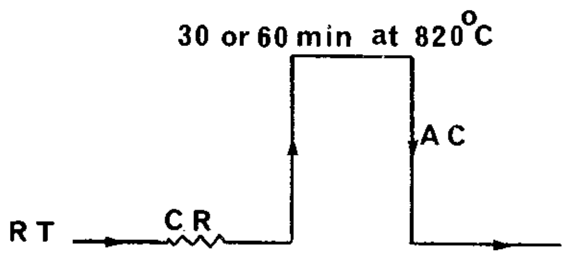
(ii) Prior γ grain size, ~ 300 μm.

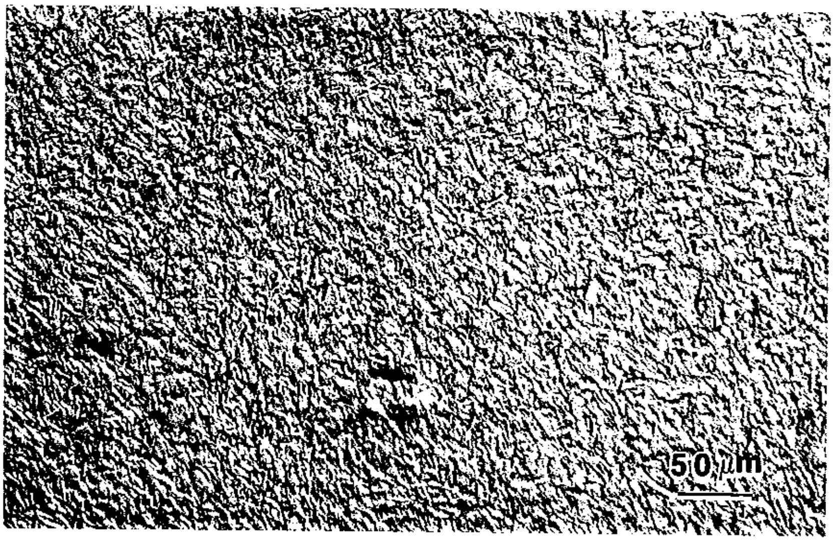
(iii) Inclusions ranging in size from 0.1 - 1 μm.

FIGURE 1. MAR 350, COLD ROLLED


1 μm


1 μm



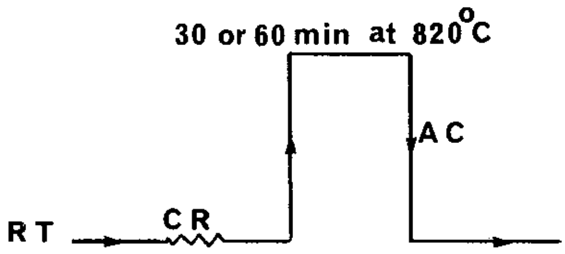


OBSERVATIONS

(i) Recrystallisation has occurred.

(ii) Inclusions are present (arrowed).

FIGURE 2. MAR 350, 820°C FOR 30 MINUTES

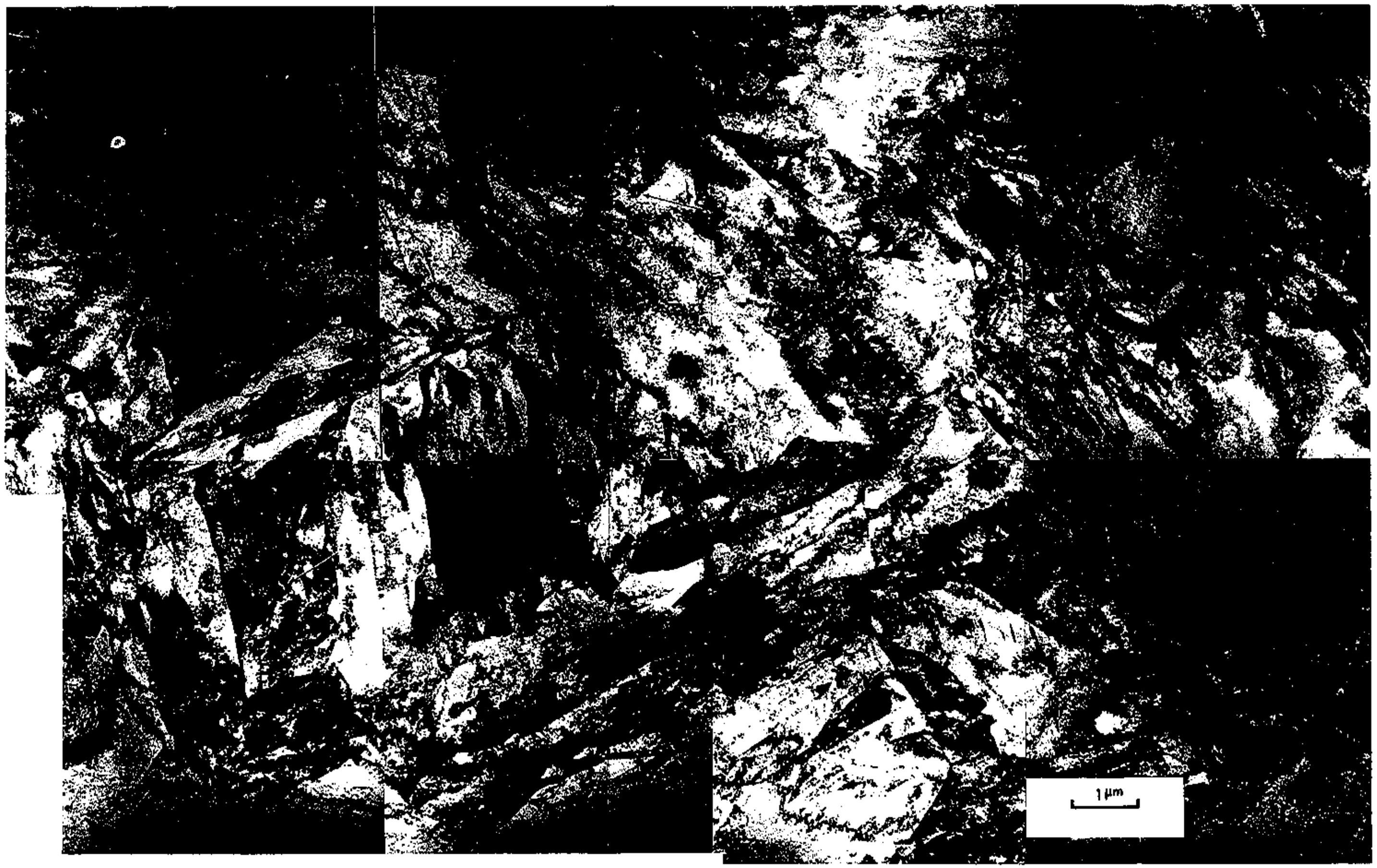


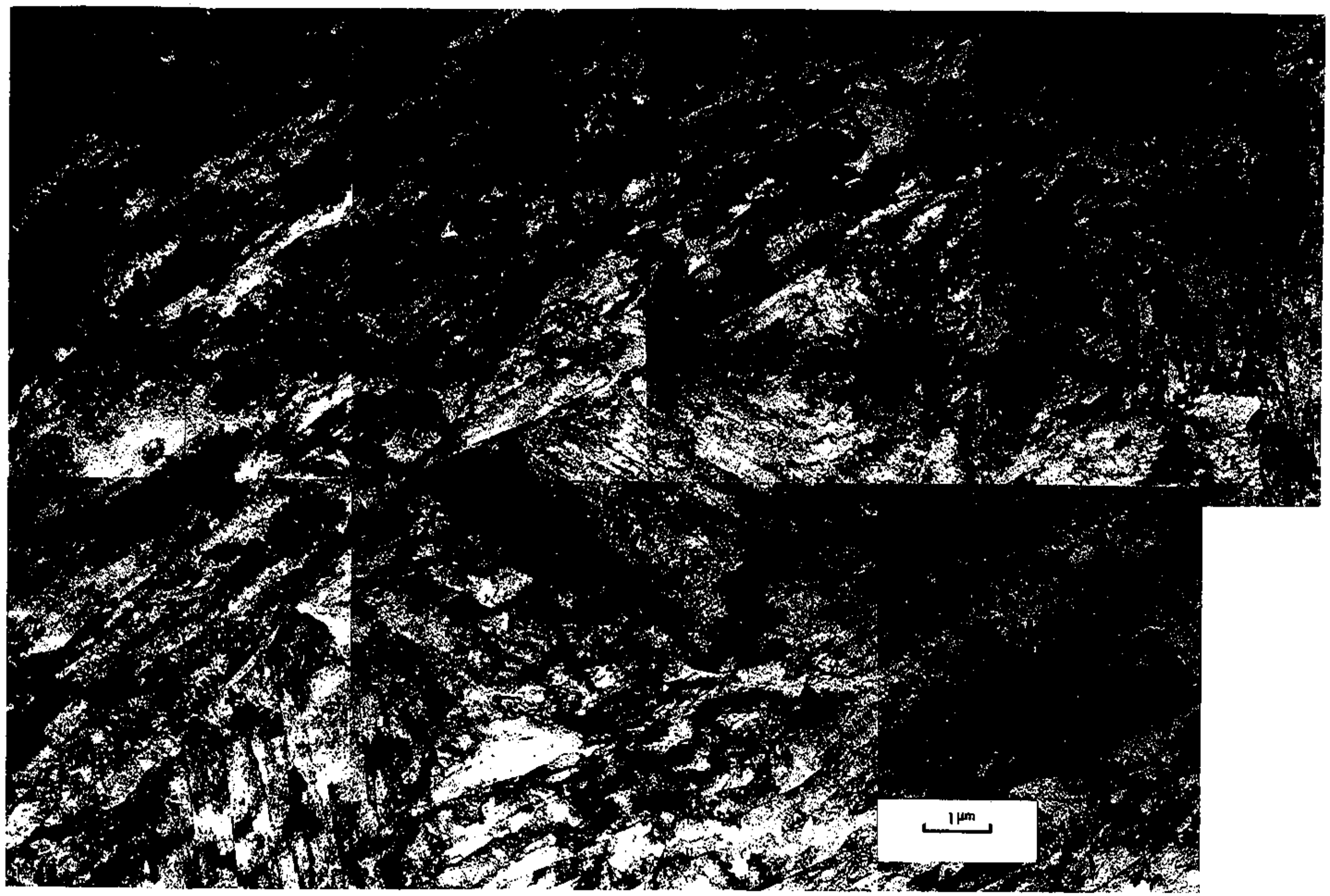
OBSERVATIONS

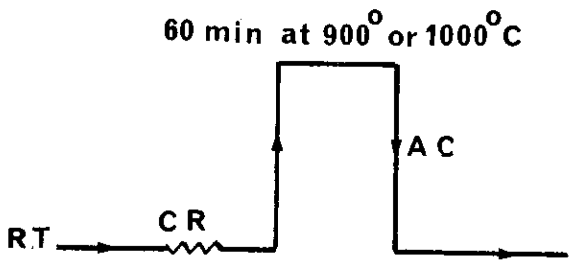
(i) Recrystallisation is complete. Grain size ~ 25 μm.

(ii) Only large inclusions remain (arrowed).

FIGURE 3. MAR 350, 820°C FOR 60 MINUTES


1 μm


1 µm

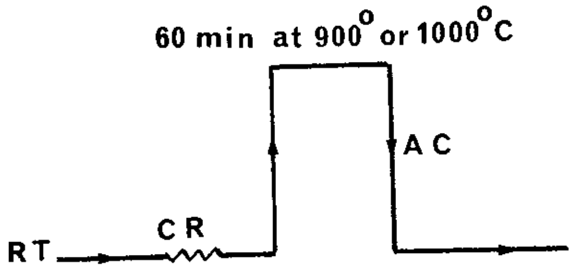


OBSERVATIONS

(i) Well recrystallised structure having moderate grain size ~ 60 μm.

(ii) Only large occasional inclusions remain.

FIGURE 4. MAR 350, 900°C FOR 60 MINUTES



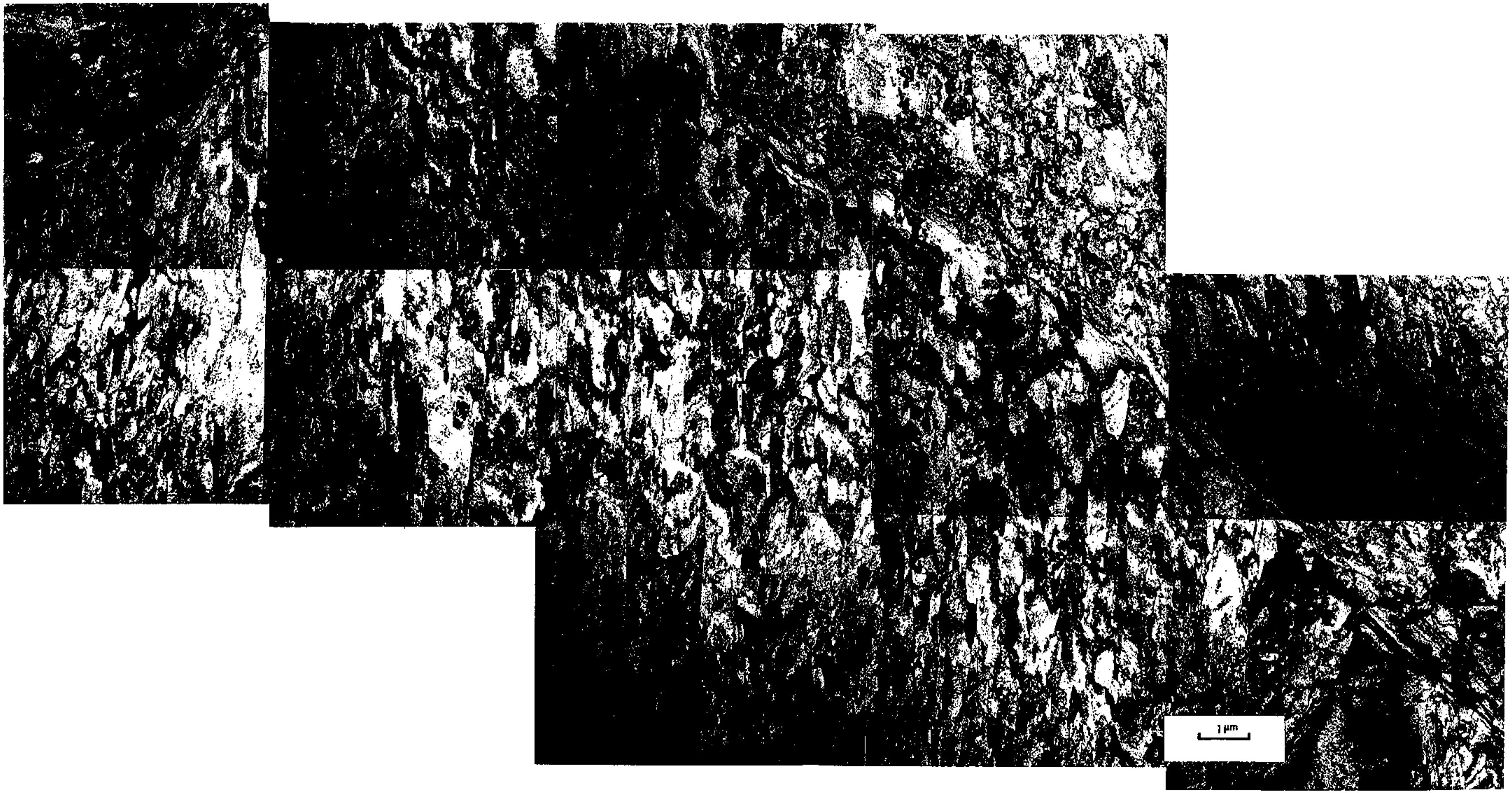
OBSERVATIONS

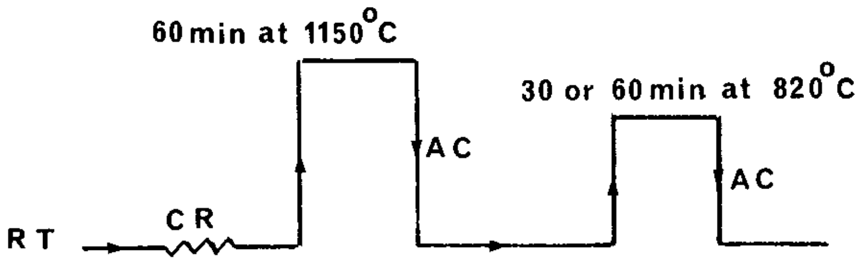
(i) Recrystallised grain size ~ 125 μm.

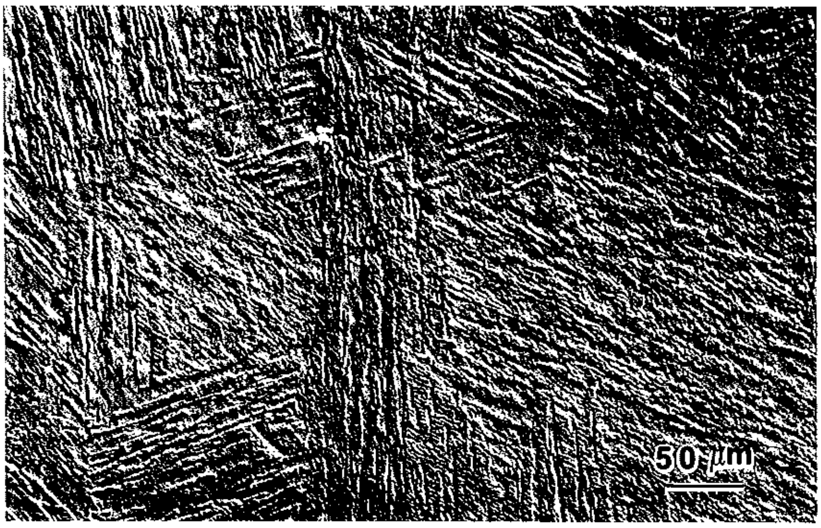
(ii) Large isolated inclusions remain.

FIGURE 5. MAR 350, 1000°C FOR 60 MINUTES


1 µm


1 μm





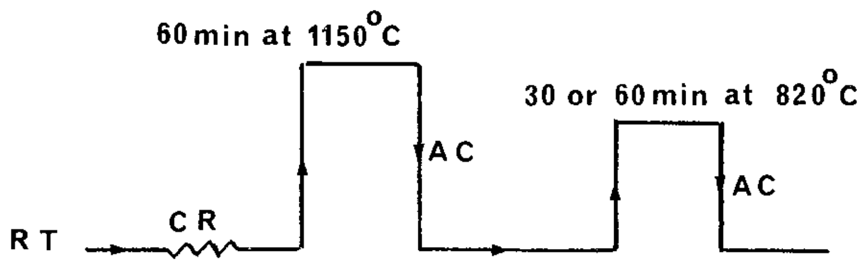
OBSERVATIONS

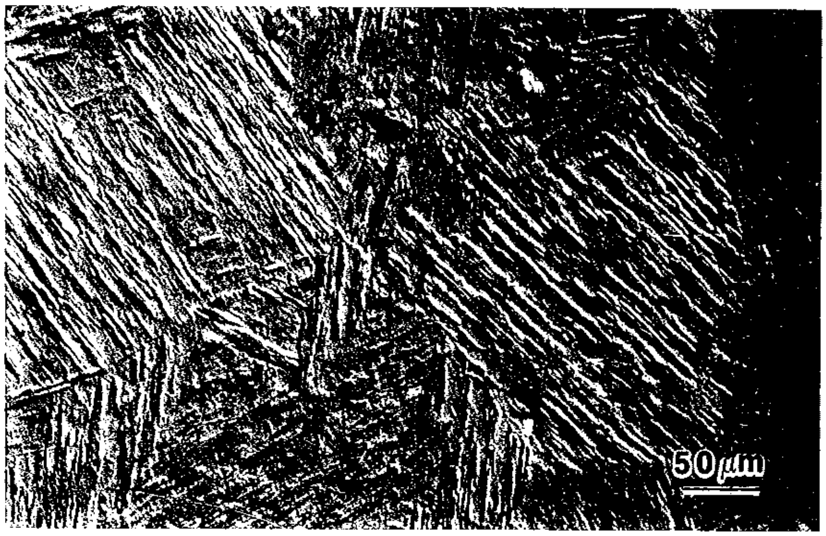
(i) Large grain size ~ 250 μm.

(ii) Only occasional inclusions.

(iii) Very sharply defined lath boundaries.

FIGURE 6. MAR 350, 1150°C FOR 60 MINUTES FOLLOWED BY 820°C FOR 30 MINUTES





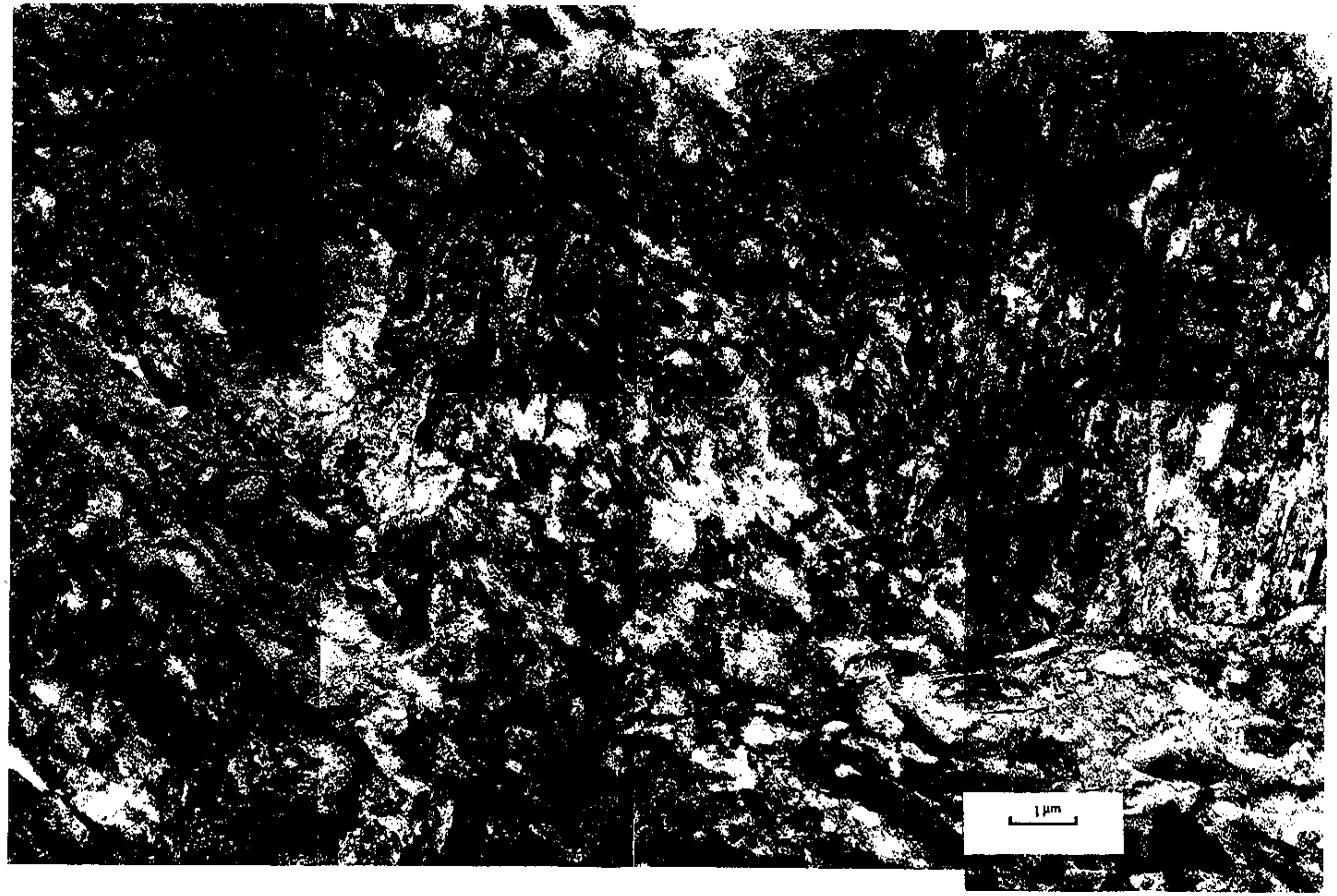
OBSERVATIONS

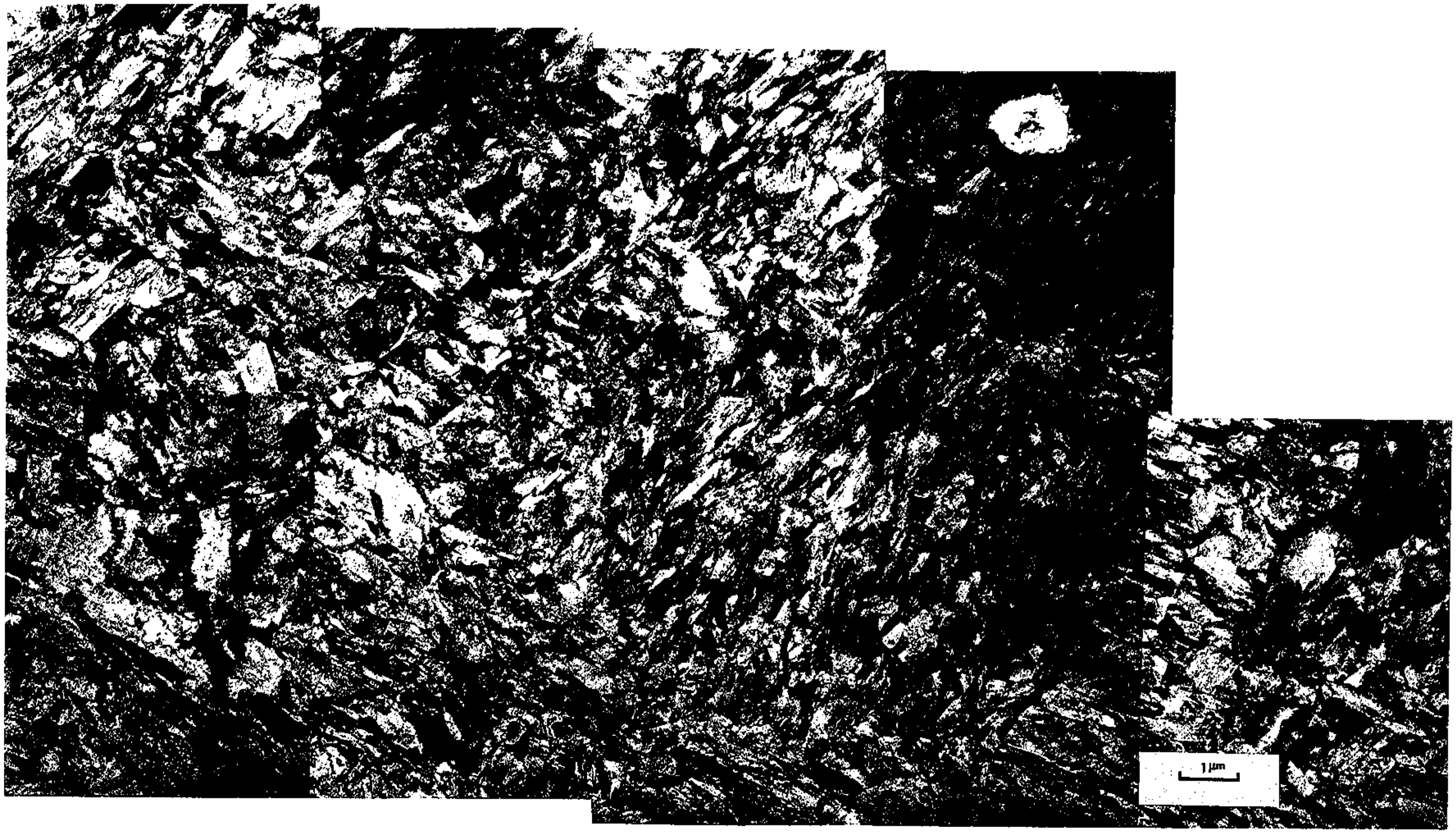
(i) Large recrystallised grain size ~ 250 μm, identical with that of Figure 6, confirming that it results from the 1150°C treatment.

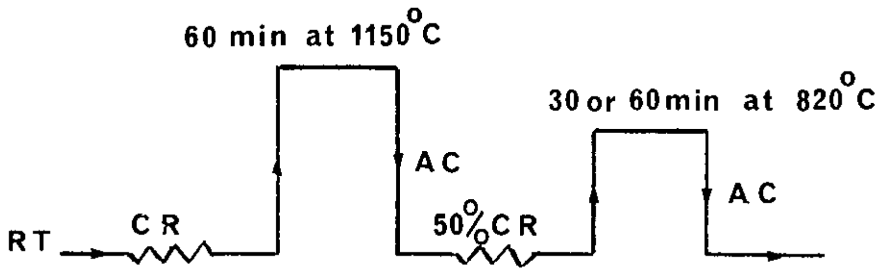
(ii) Very few inclusions observed.

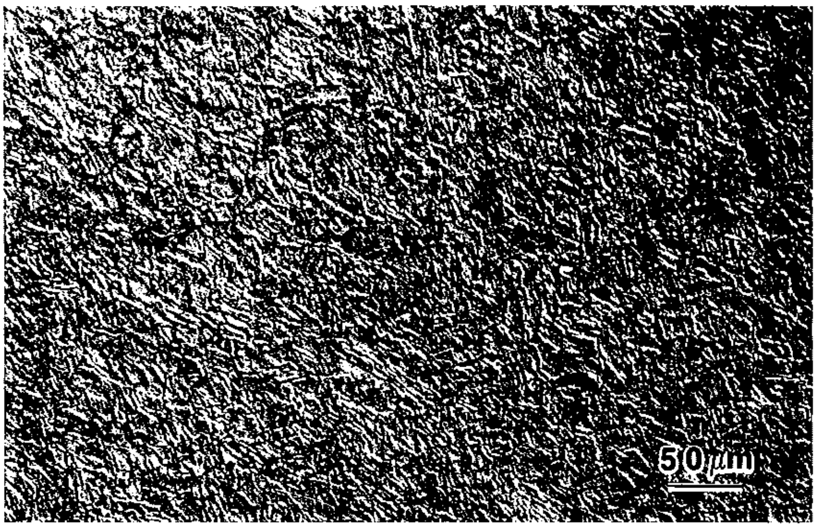
(iii) Well defined lath boundaries.

FIGURE 7. MAR 350, 1150°C FOR 60 MINUTES FOLLOWED BY 820°C FOR 60 MINUTES


1 µm


1 μm



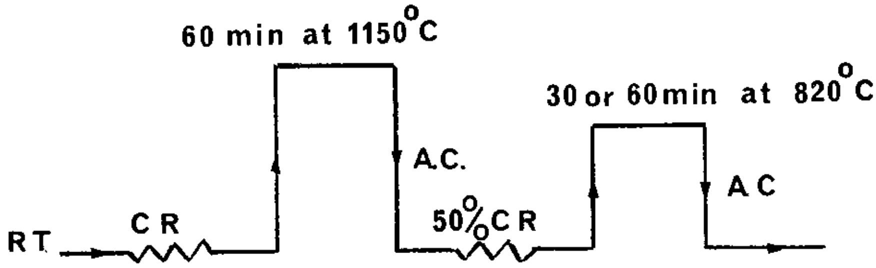


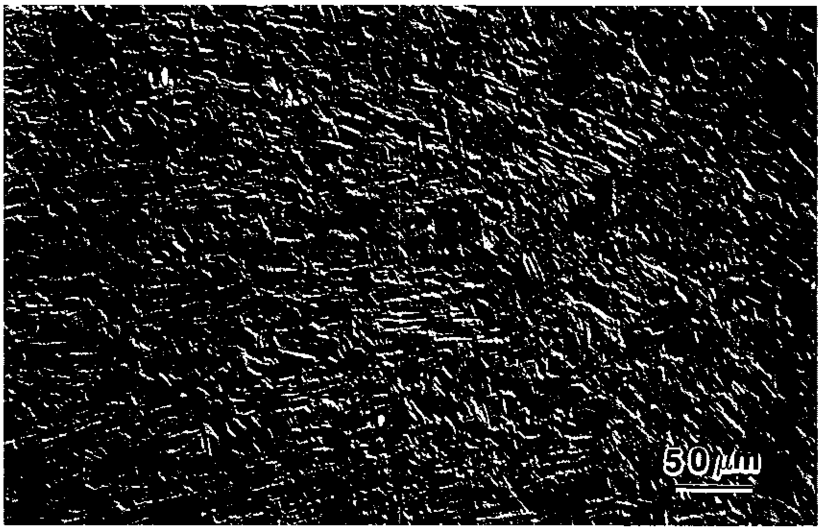
OBSERVATIONS

(i) Small recrystallised grain size ~ 15 μm.

(ii) Some inclusions.

FIGURE 8. MAR 350, 1150°C FOR 60 MINUTES, FOLLOWED BY 50% COLD REDUCTION AND 30 MINUTES AT 820°C



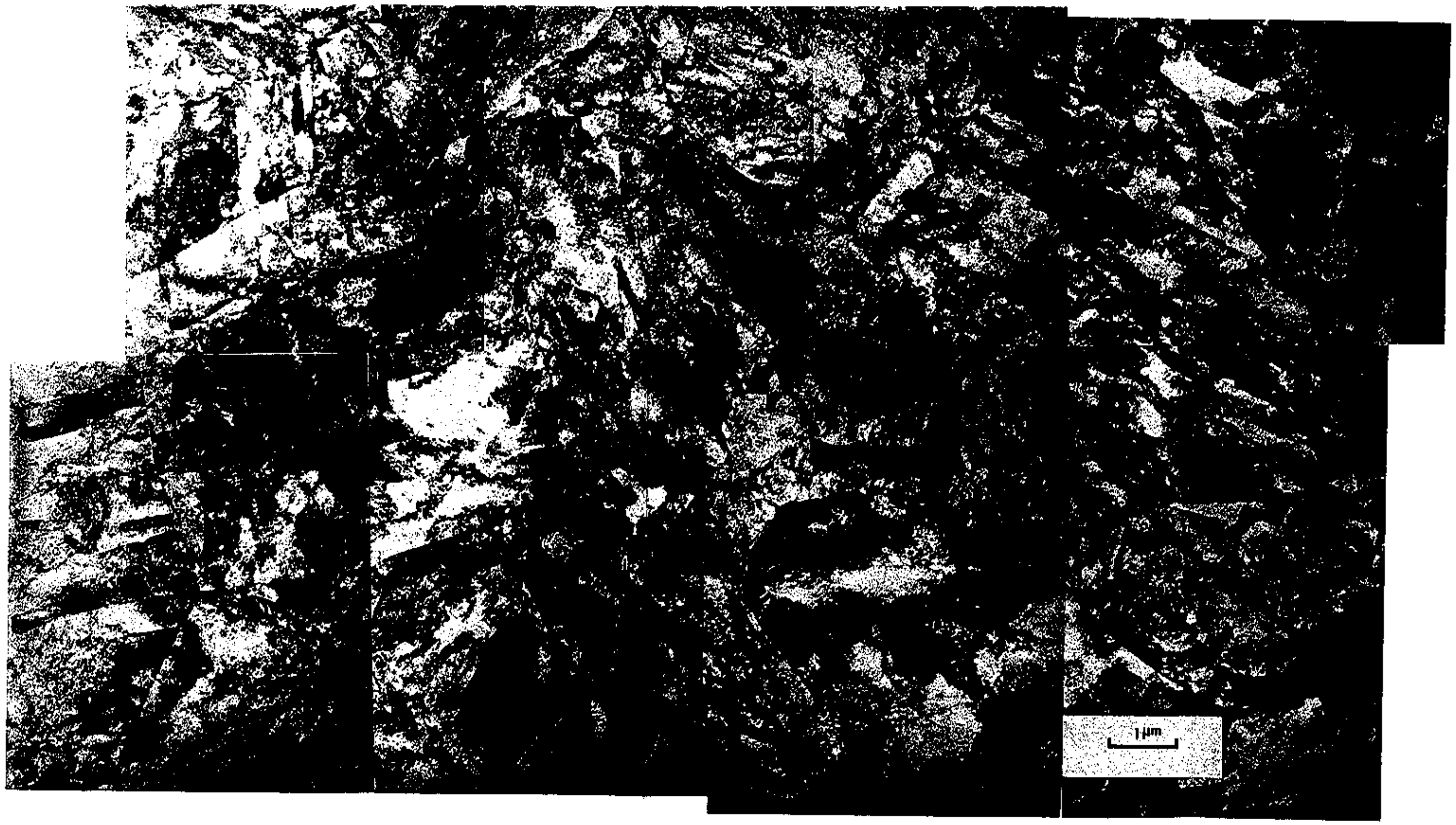


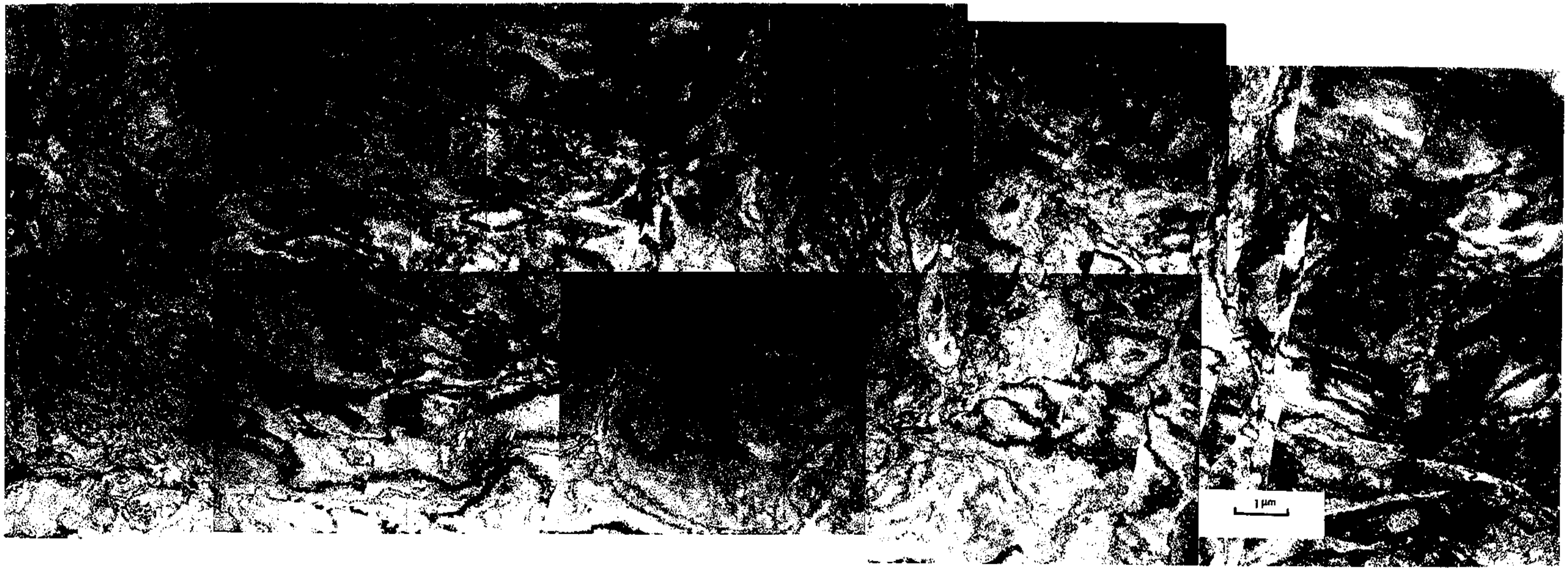
OBSERVATIONS

(i) Small recrystallised grain size ~ 25 μm.

(ii) A few large black spots of unknown origin are observed.

FIGURE 9. MAR 350, 1150°C FOR 60 MINUTES, FOLLOWED BY 50% COLD REDUCTION AND 60 MINUTES AT 820°C


1μm


1 µm

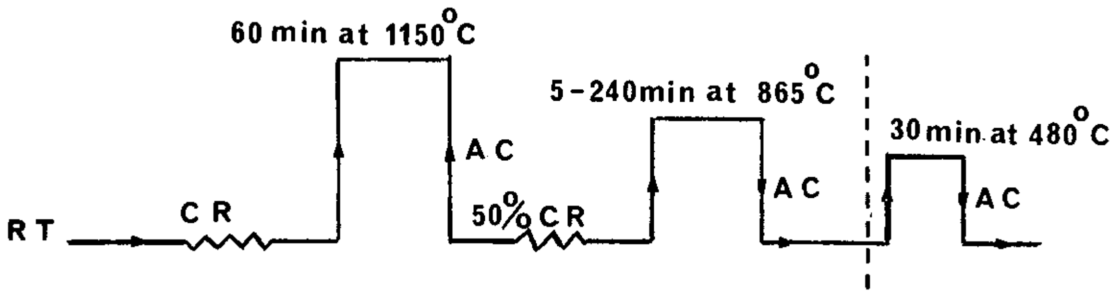
OBSERVATIONS

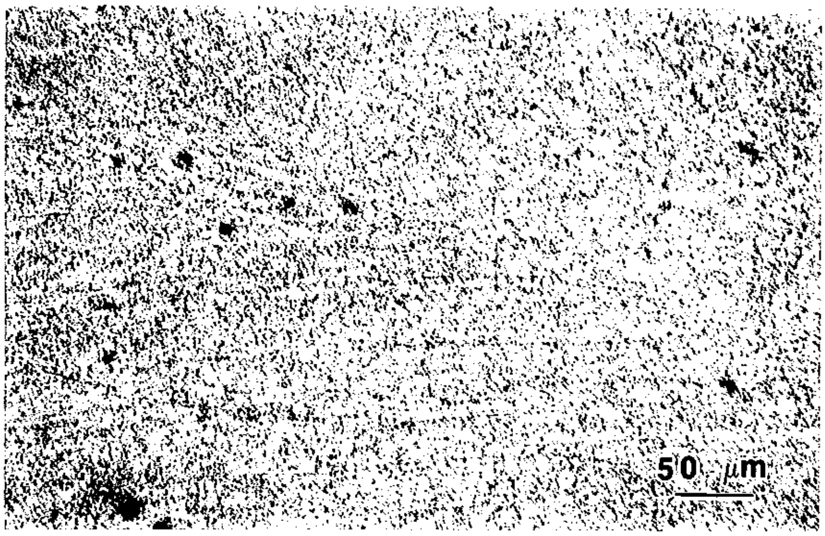
(i) Deformed structure.

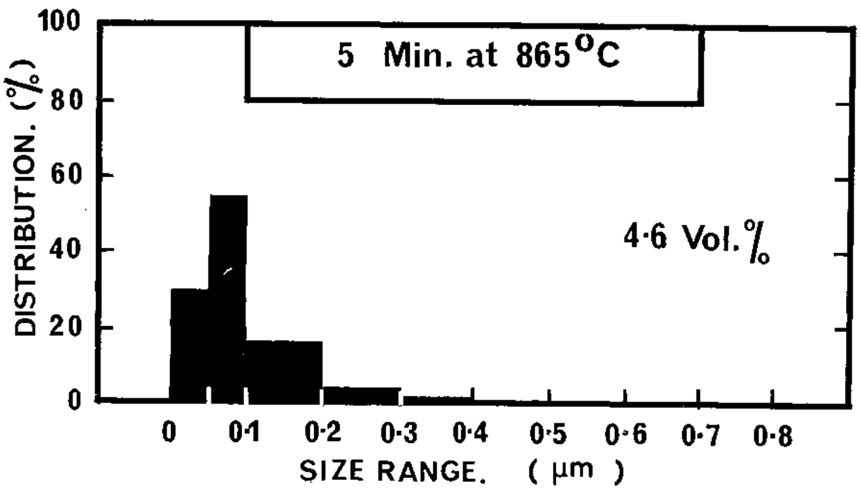
(ii) Large grain size ~ 150 μm.

(iii) Large inclusions noted.

FIGURE 10. MAR 400, HOMOGENISED AT 1150°C FOR 1 HOUR, FOLLOWED BY 50% COLD REDUCTION







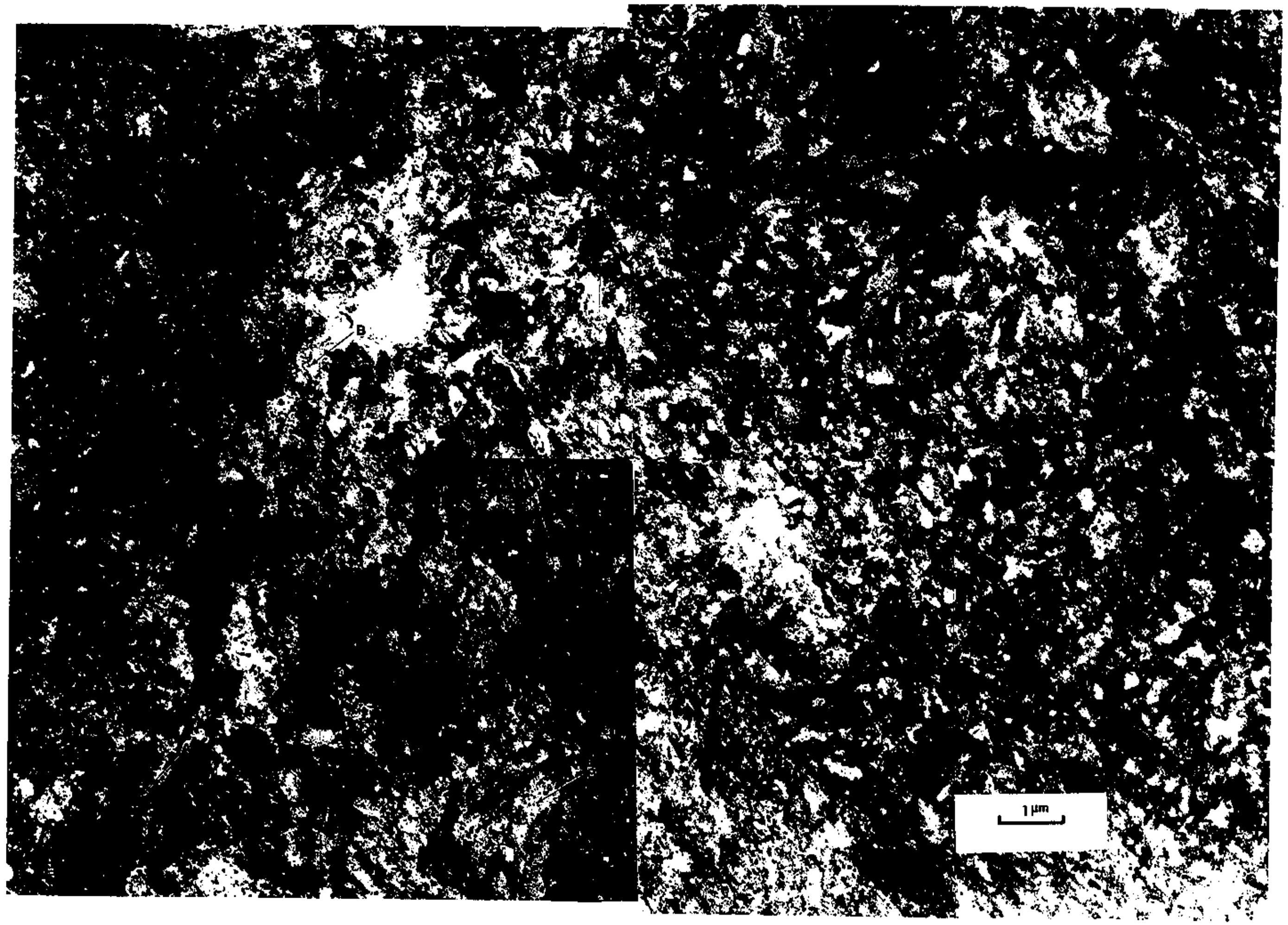
<u>OBSERVATIONS</u>

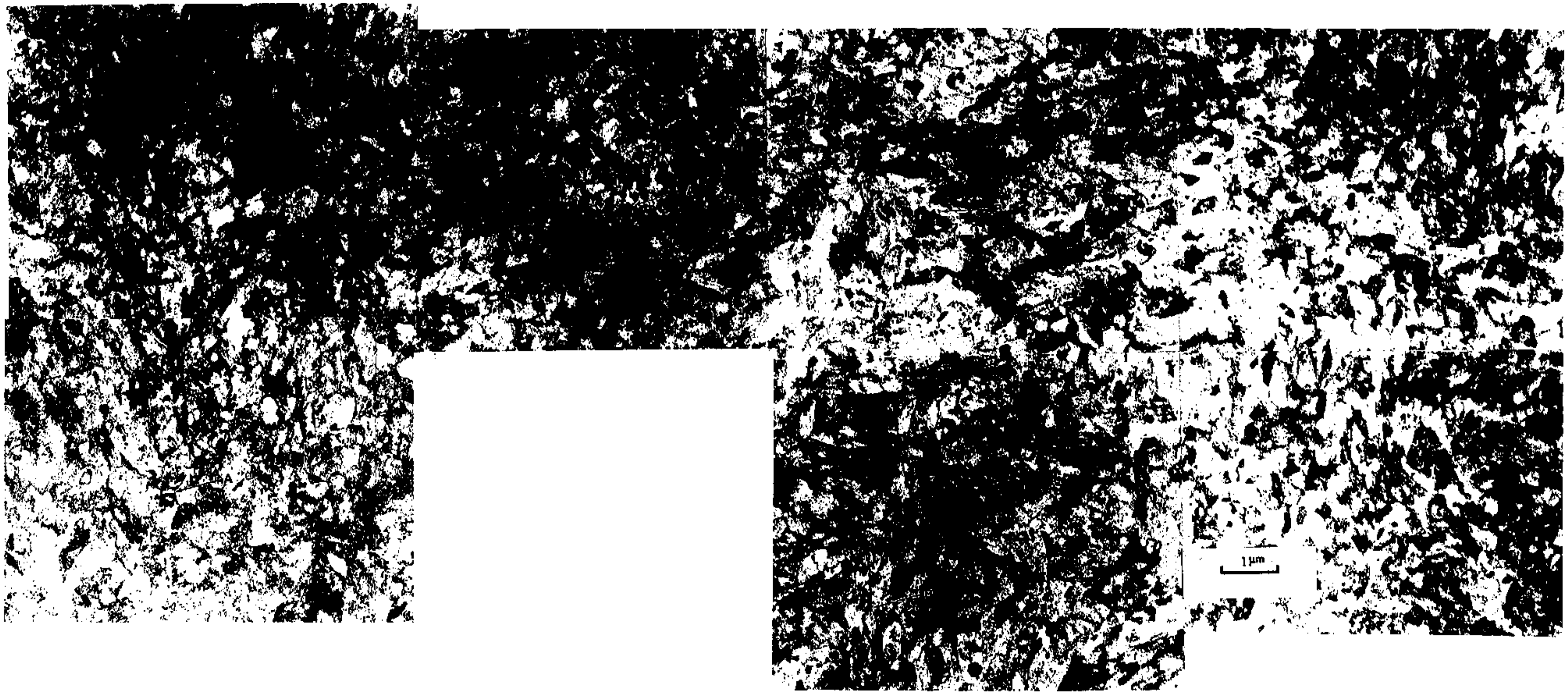
(i) The specimen has not recrystallised. Heavily deformed grains are evident.

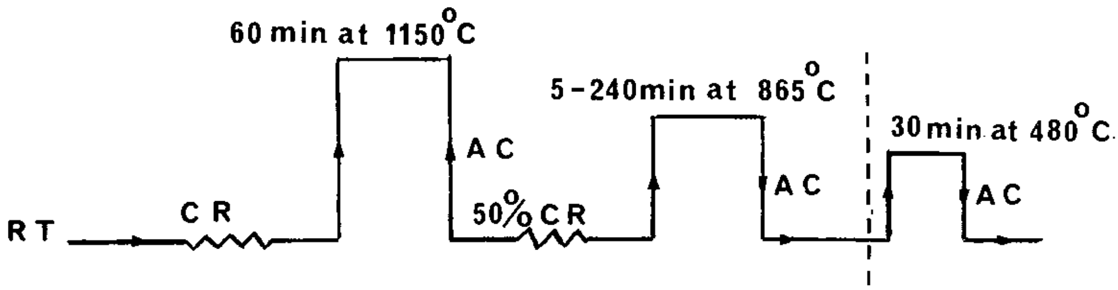
(ii) Two types of precipitate are observed. Type A (arrowed) has been identified by electron-diffraction as a μ-phase having the composition $(FeCo)_7$. A smaller more rounded precipitate, type B (arrowed), has not been identified.

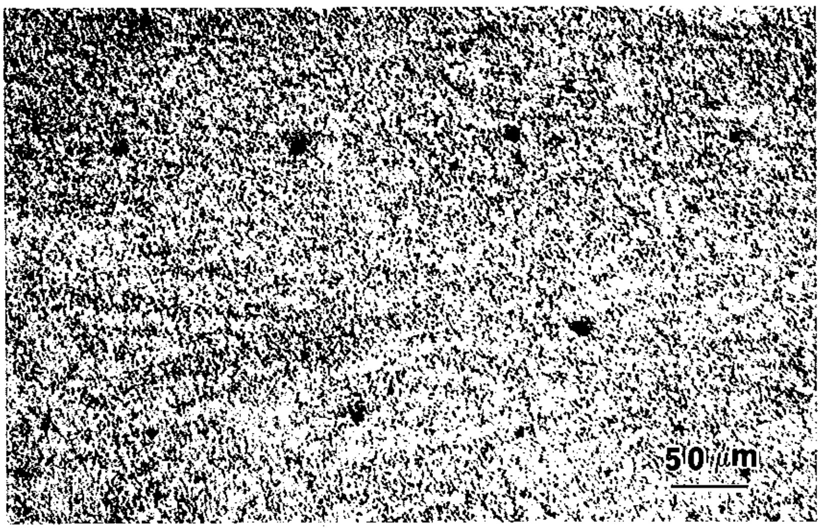
(iii) Precipitate size ranges to 0.3 μm average diameter. The highest fractions are in the smallest size ranges and are mainly type B.

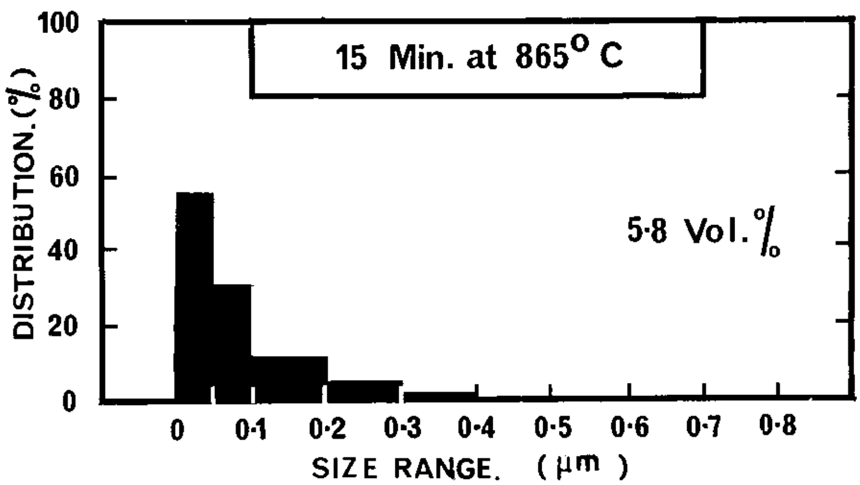
FIGURE 11. MAR 400, 5 MINUTES AT 865°C


B
1 µm


1 μm







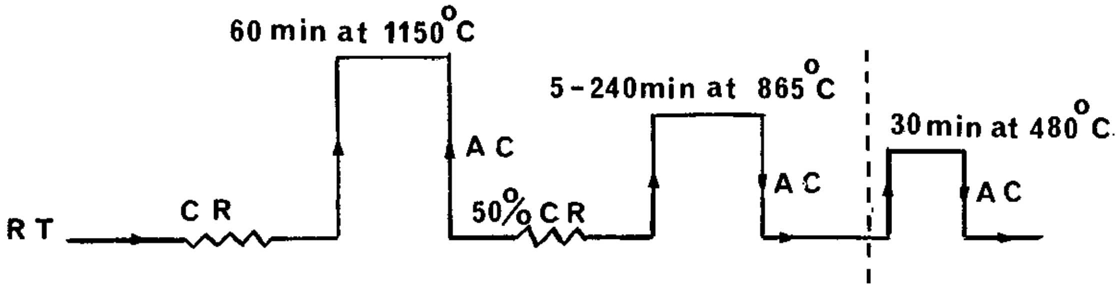
OBSERVATIONS

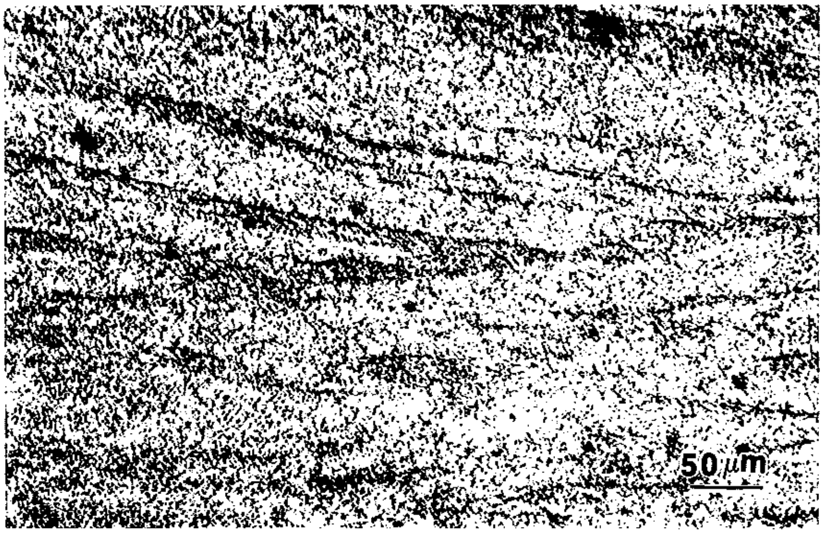
(i) The specimen has not been recrystallised. Deformation is observed.

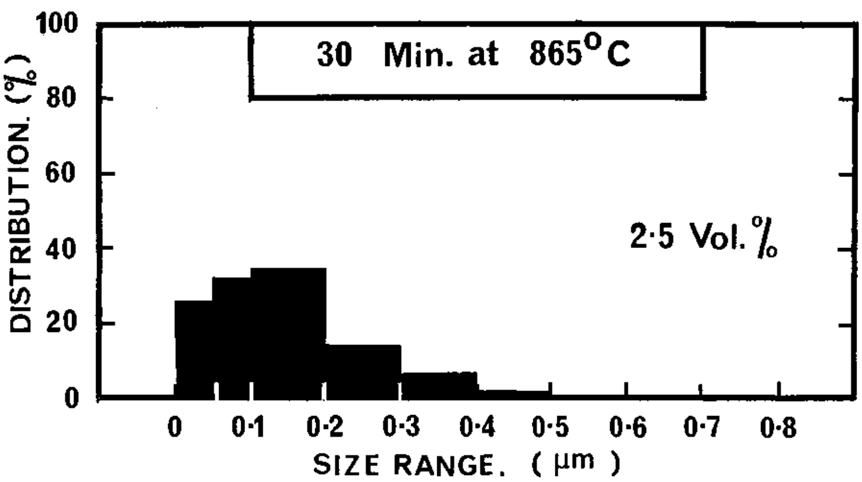
(ii) Both type A (arrowed) and type B (arrowed) precipitates are observed.

(iii) Precipitate size ranges to 0.4 μm average diameter. The highest fraction is in the smallest size ranges and is overwhelmingly type B.

FIGURE 12. MAR 400, 15 MINUTES AT 865°C







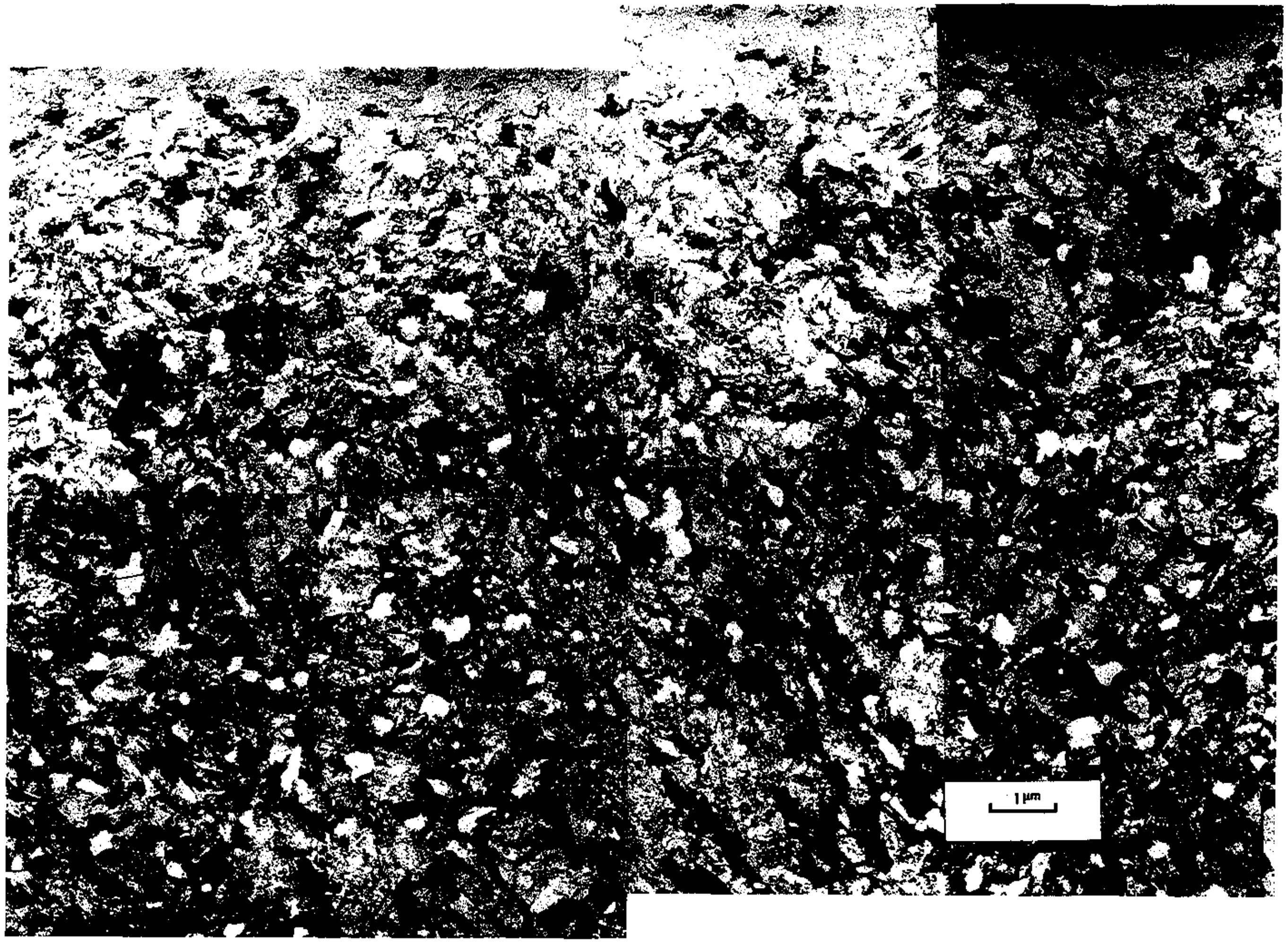
OBSERVATIONS

(i) Specimen has not recrystallised.

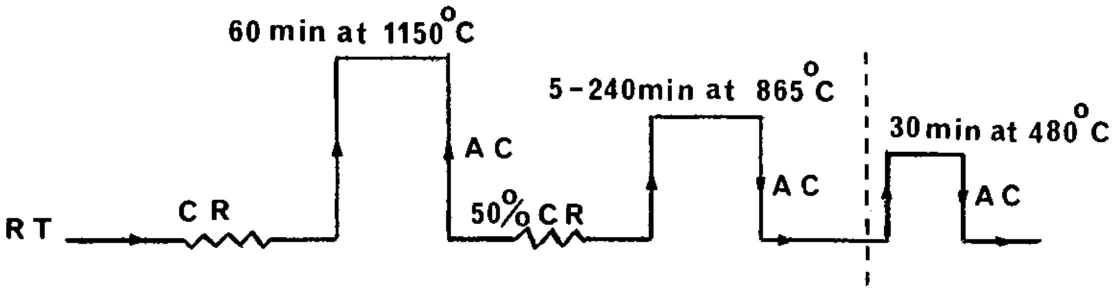
(ii) Type A (arrowed) and type B (arrowed) precipitates are observed.

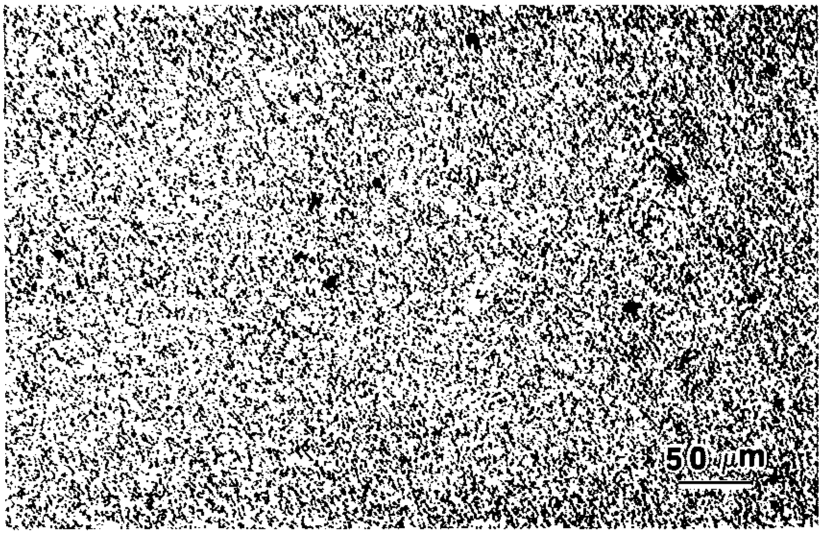
(iii) Precipitate size ranges to 0.5 µm average diameter. The largest size fraction is no longer in the smaller size ranges.

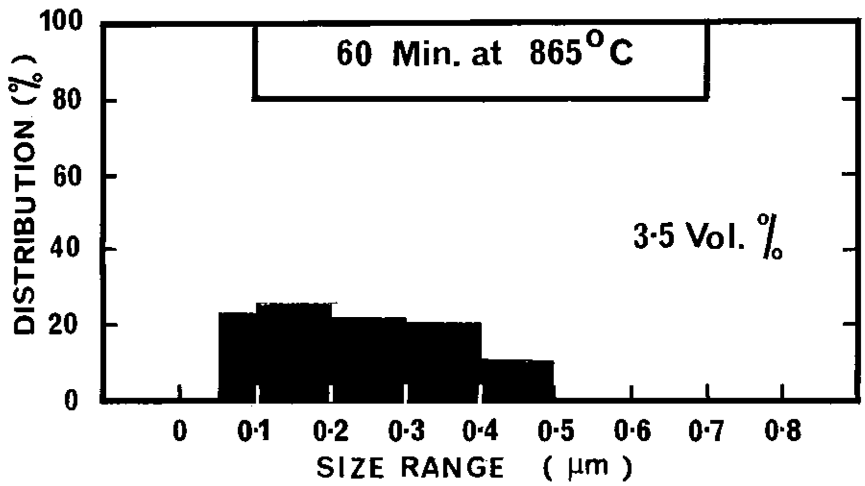
FIGURE 13. MAR 400, 30 MINUTES AT 865°C


1 μm


1 μm







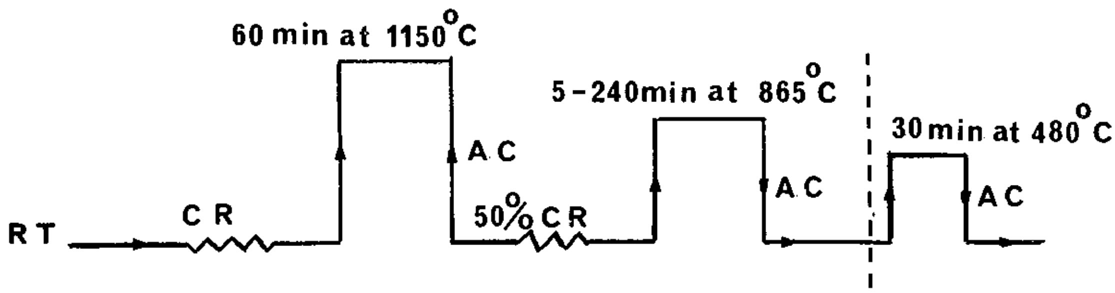
<u>OBSERVATIONS</u>

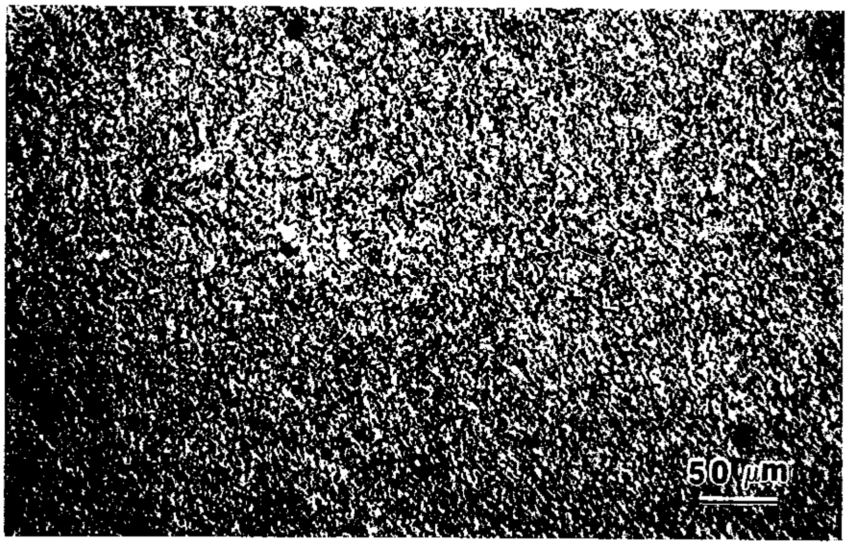
(i) Specimen has not recrystallised.

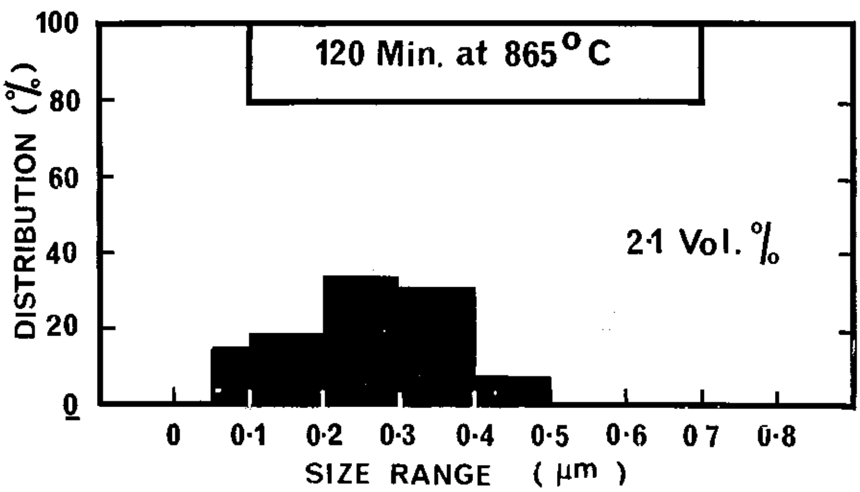
(ii) Type A (arrowed) and type B (arrowed) precipitates are still observed.

(iii) Precipitate size ranges to 0.65 µm average diameter.

FIGURE 14. MAR 400, 60 MINUTES AT 865°C







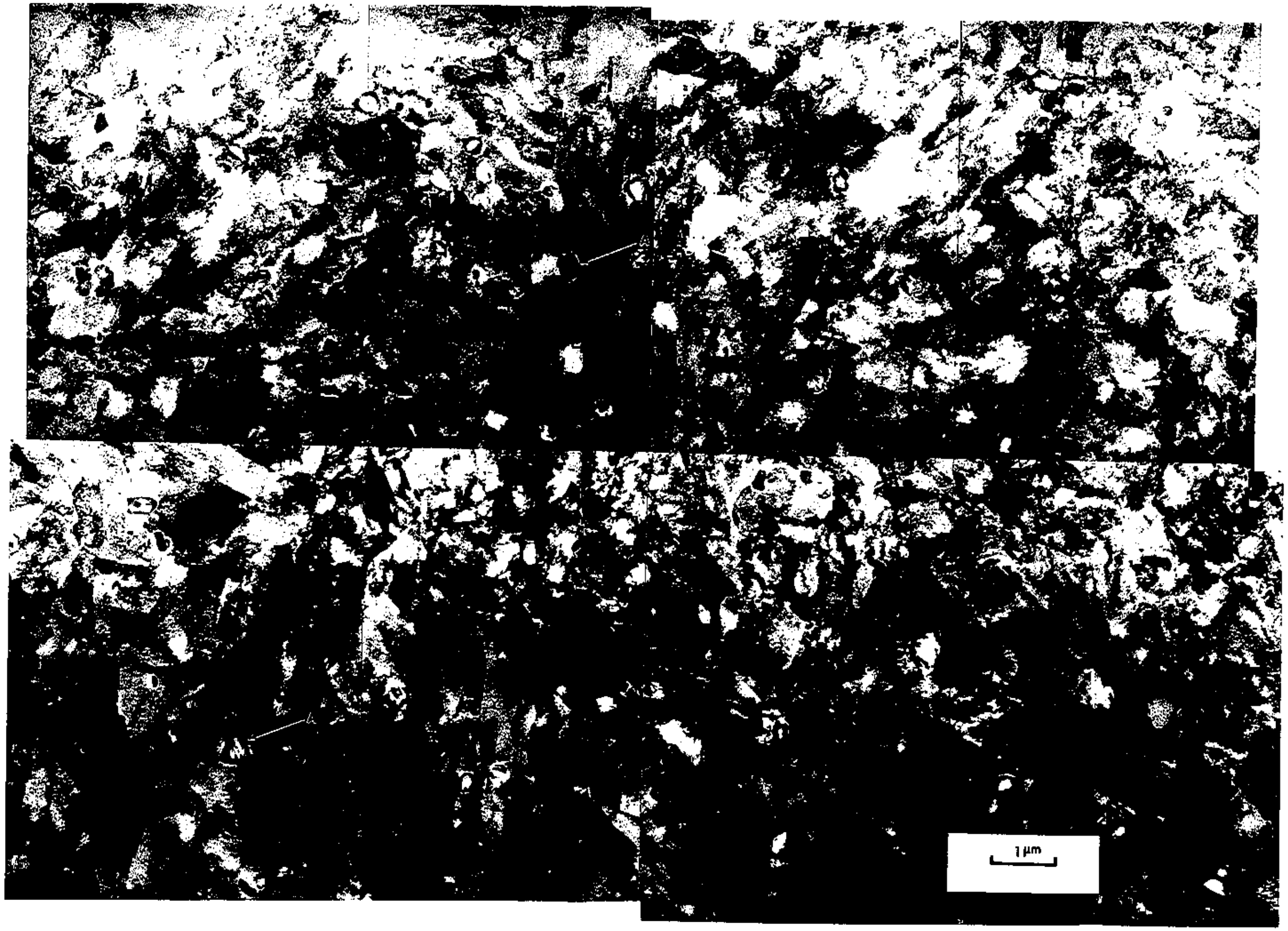
OBSERVATIONS

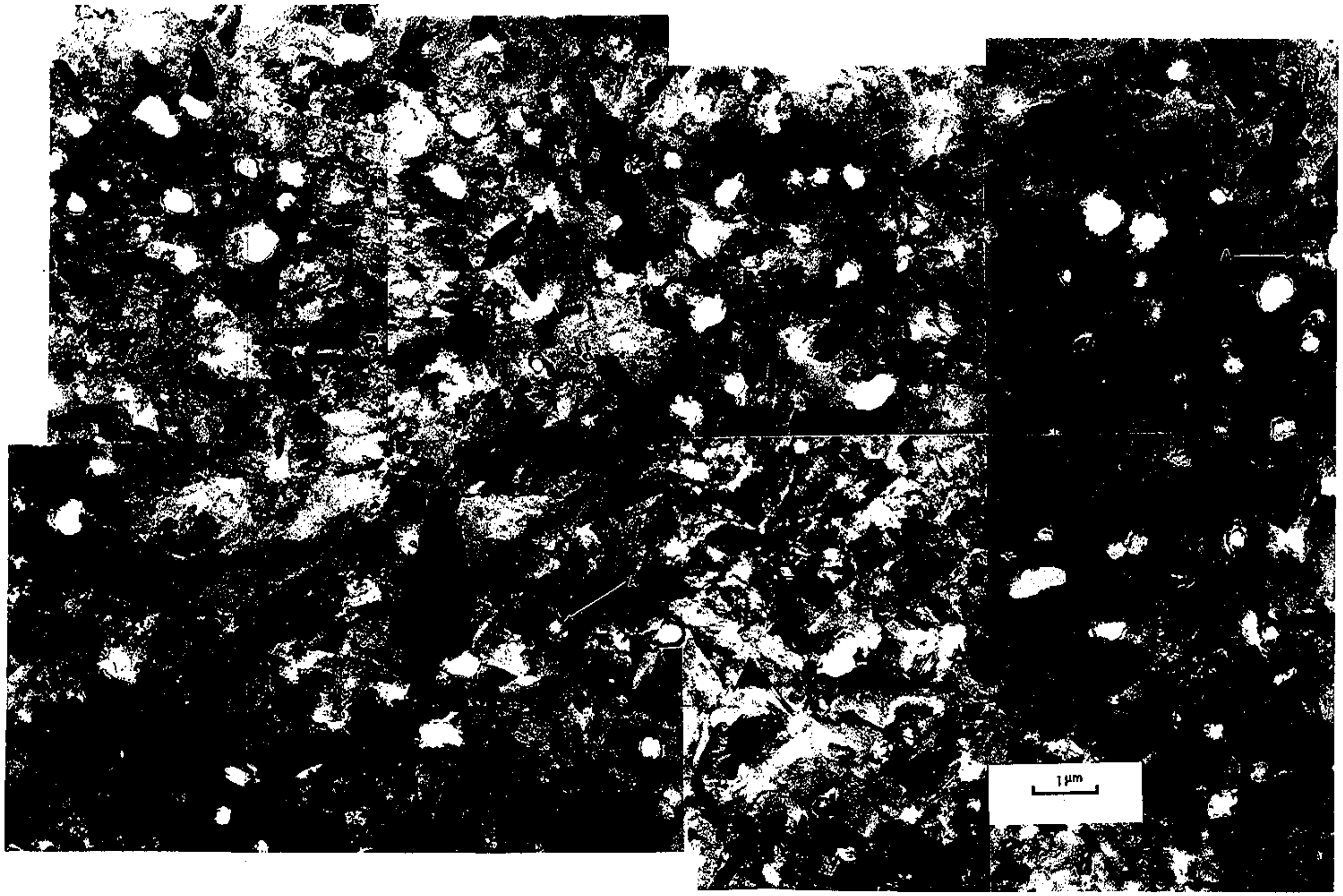
(i) Recrystallisation has not occurred.

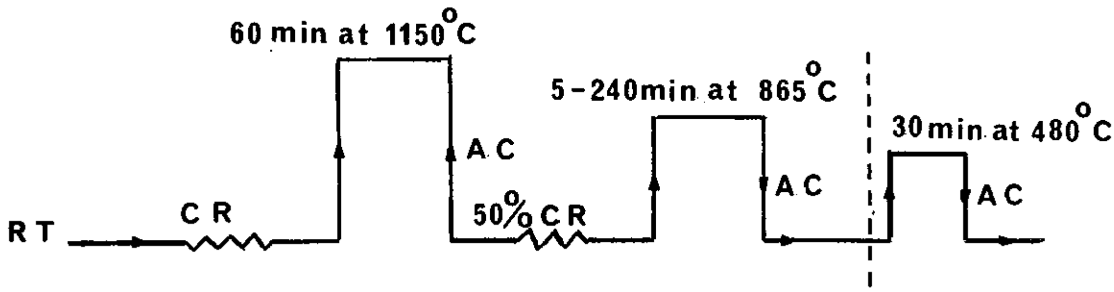
(ii) Mainly type A (arrowed) precipitates are noted. Some of these particles are heavily faulted.

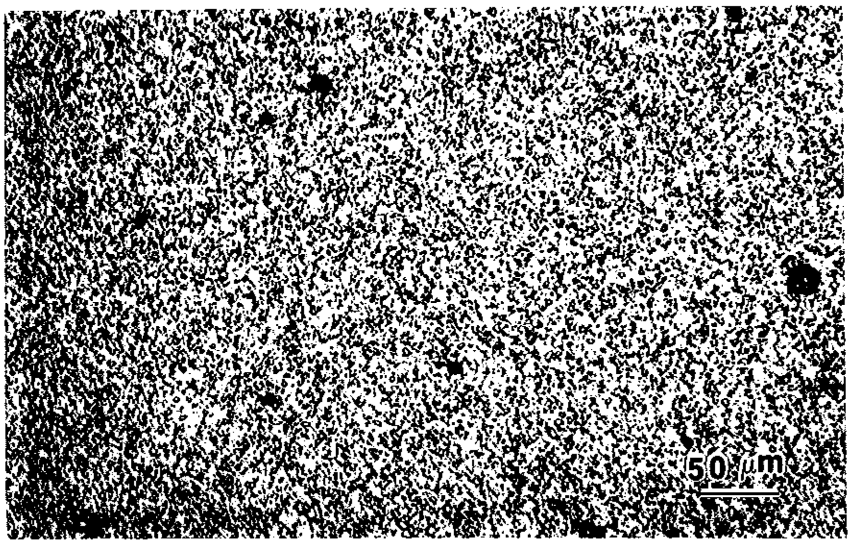
(iii) The shift in precipitate size distribution towards the larger size ranges continues.

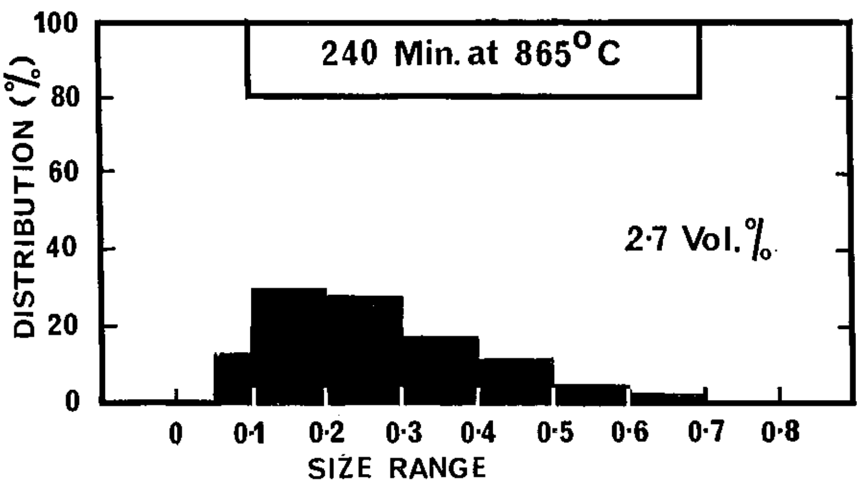
FIGURE 15. MAR 400, 120 MINUTES AT 865°C


1 μm


1 µm







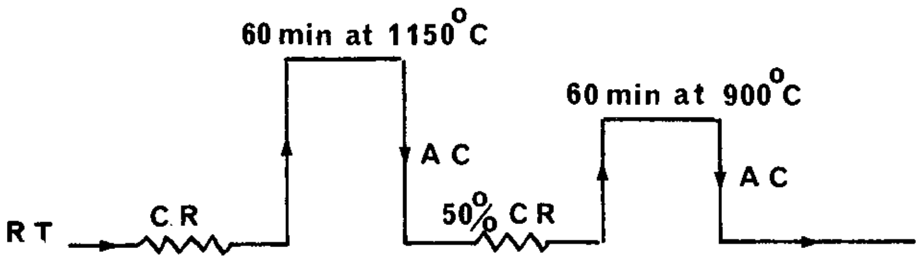
<u>OBSERVATIONS</u>

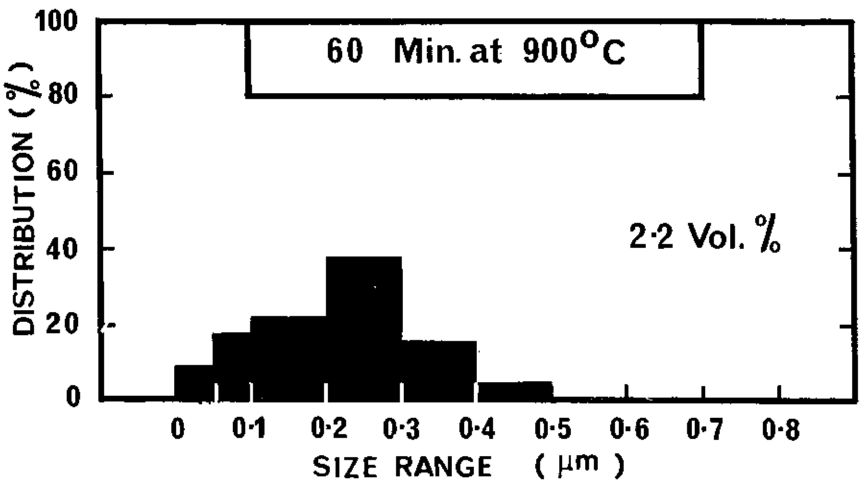
(i) Recrystallisation has not occurred. Rolling deformation is still clearly observed.

(ii) Only type A precipitates are observed.

(iii) A size distribution similar to that measured after 120 minutes at 865°C is noted.

FIGURE 16. MAR 400, 240 MINUTES AT 865°C





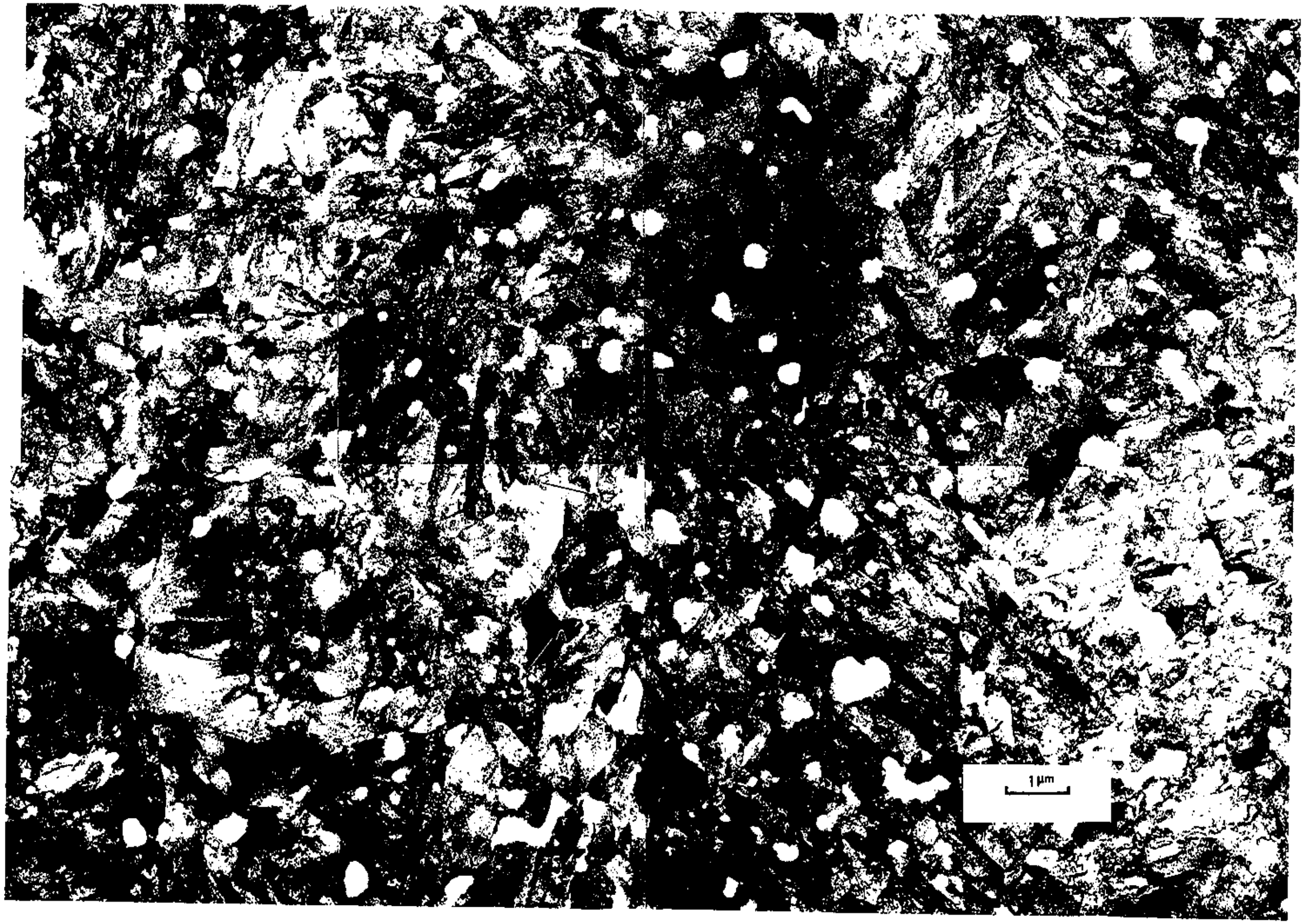
OBSERVATIONS

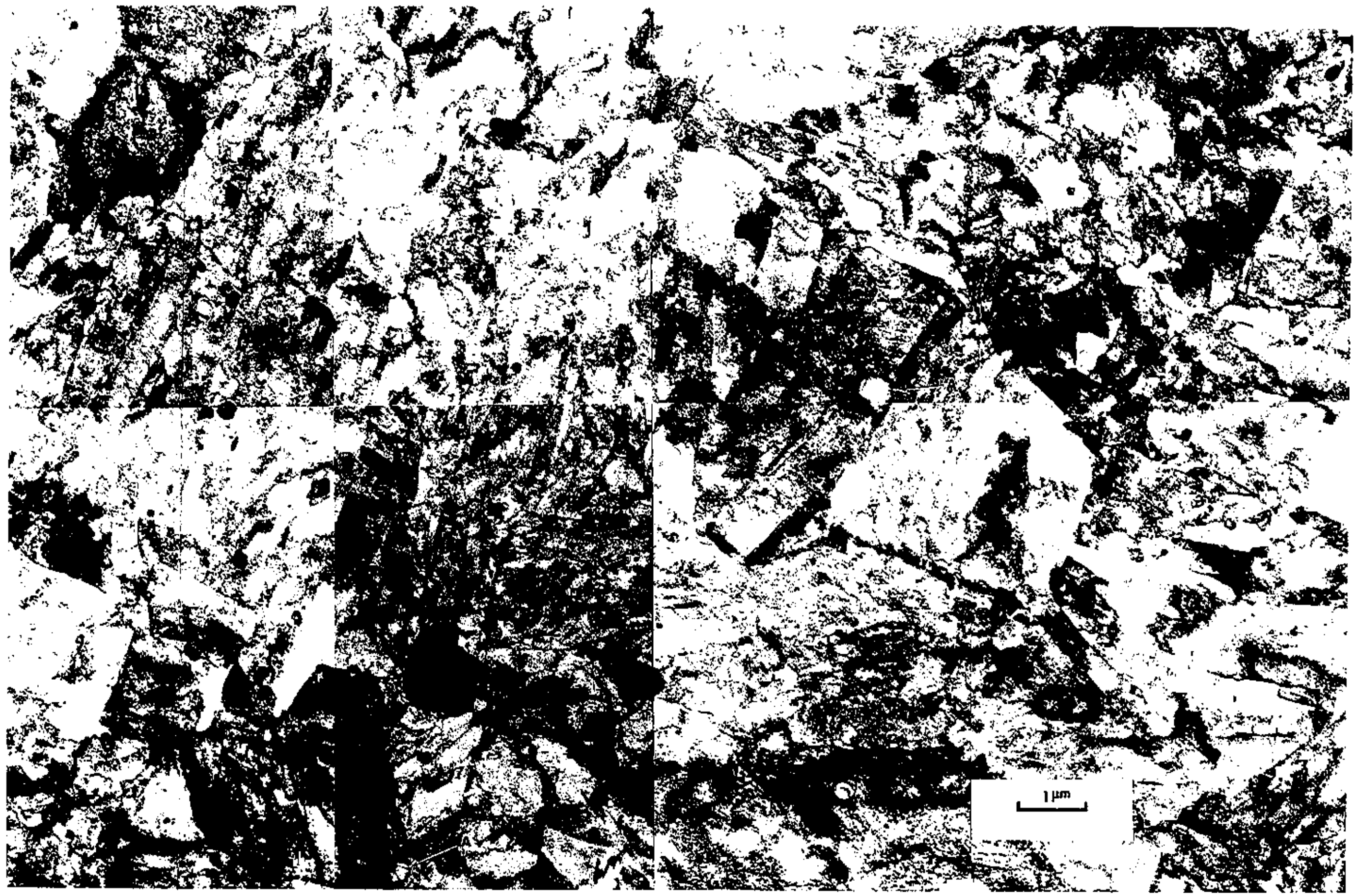
(i) Some areas of the optical micrograph show that partial recrystallisation has occurred.

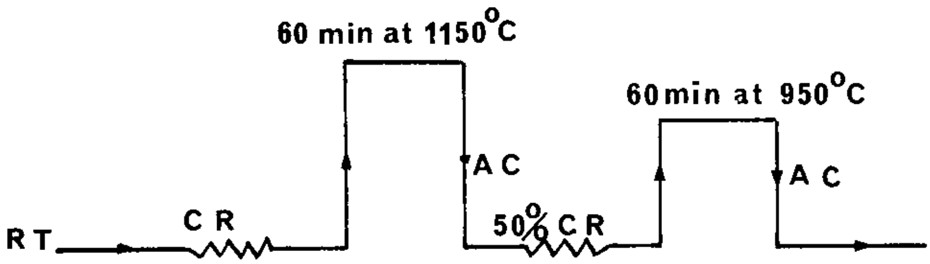
(ii) Only type A precipitates are noted.

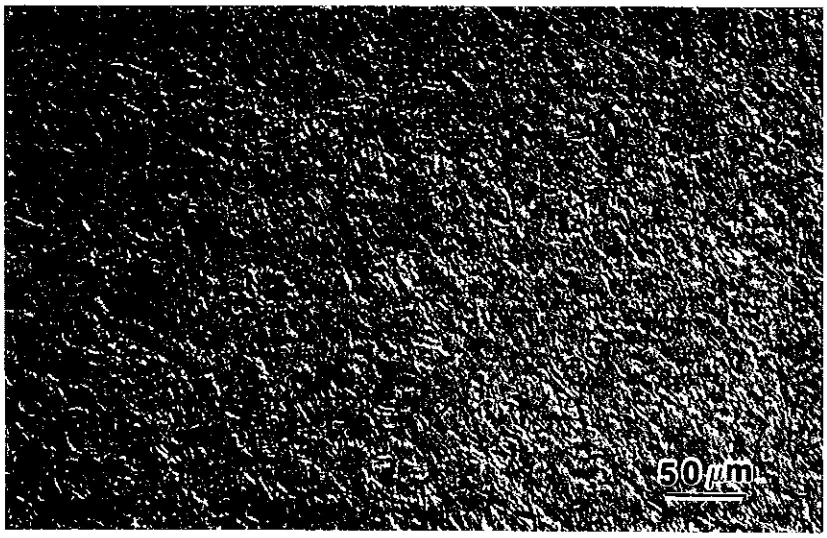
(iii) The precipitate volume (2.2 per cent) is similar to that measured after long times at 865°C.

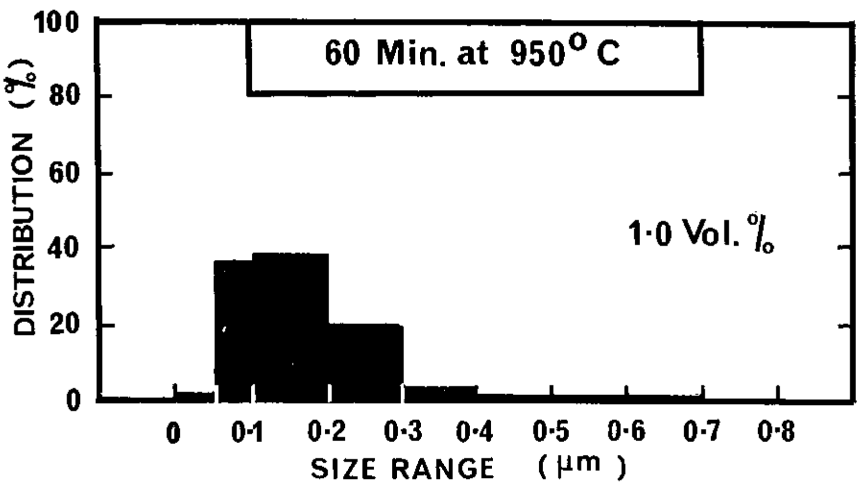
FIGURE 17. MAR 400, 60 MINUTES AT 900°C


1 µm


1 µm







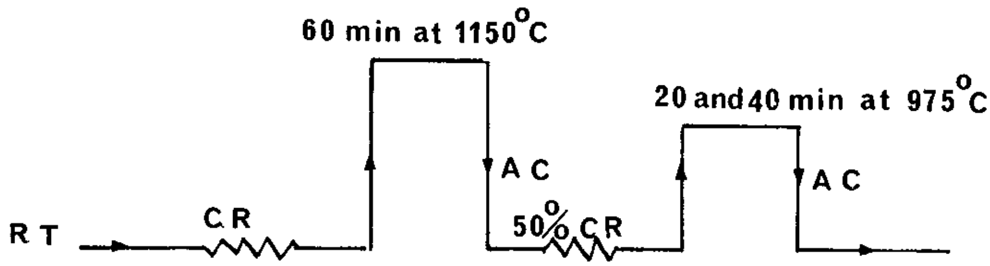
OBSERVATIONS

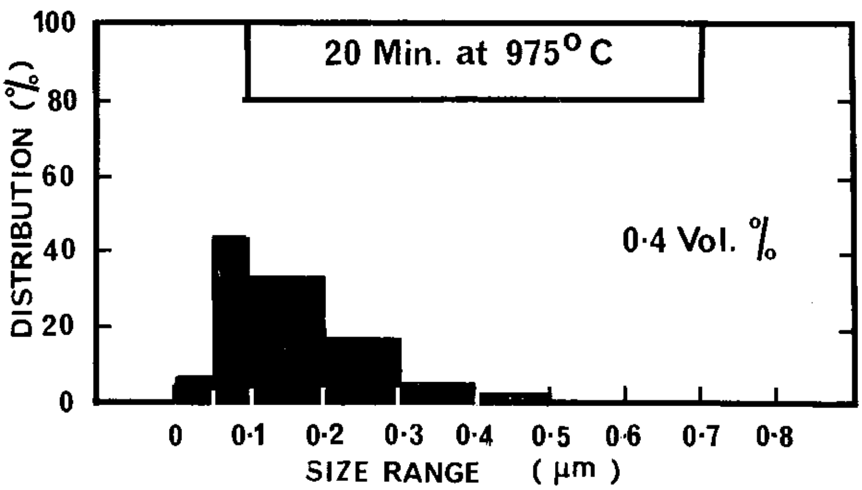
(i) Recrystallisation has occurred. The grain size is about 15 μm.

(ii) Heavily faulted type A precipitates are noted.

(iii) The volume of precipitate has fallen to 1 per cent.

FIGURE 18. MAR 400, 60 MINUTES AT 950°C





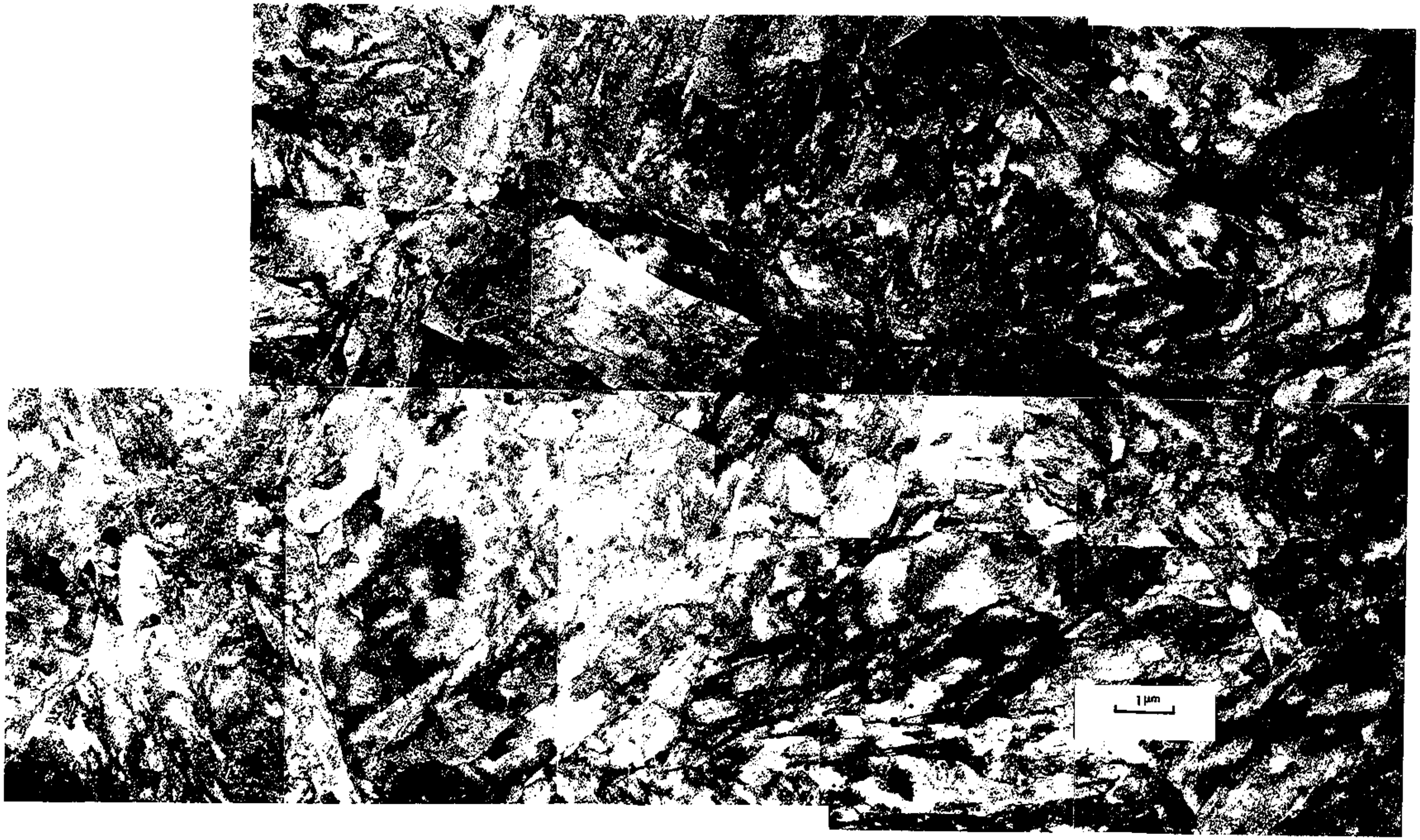
OBSERVATIONS

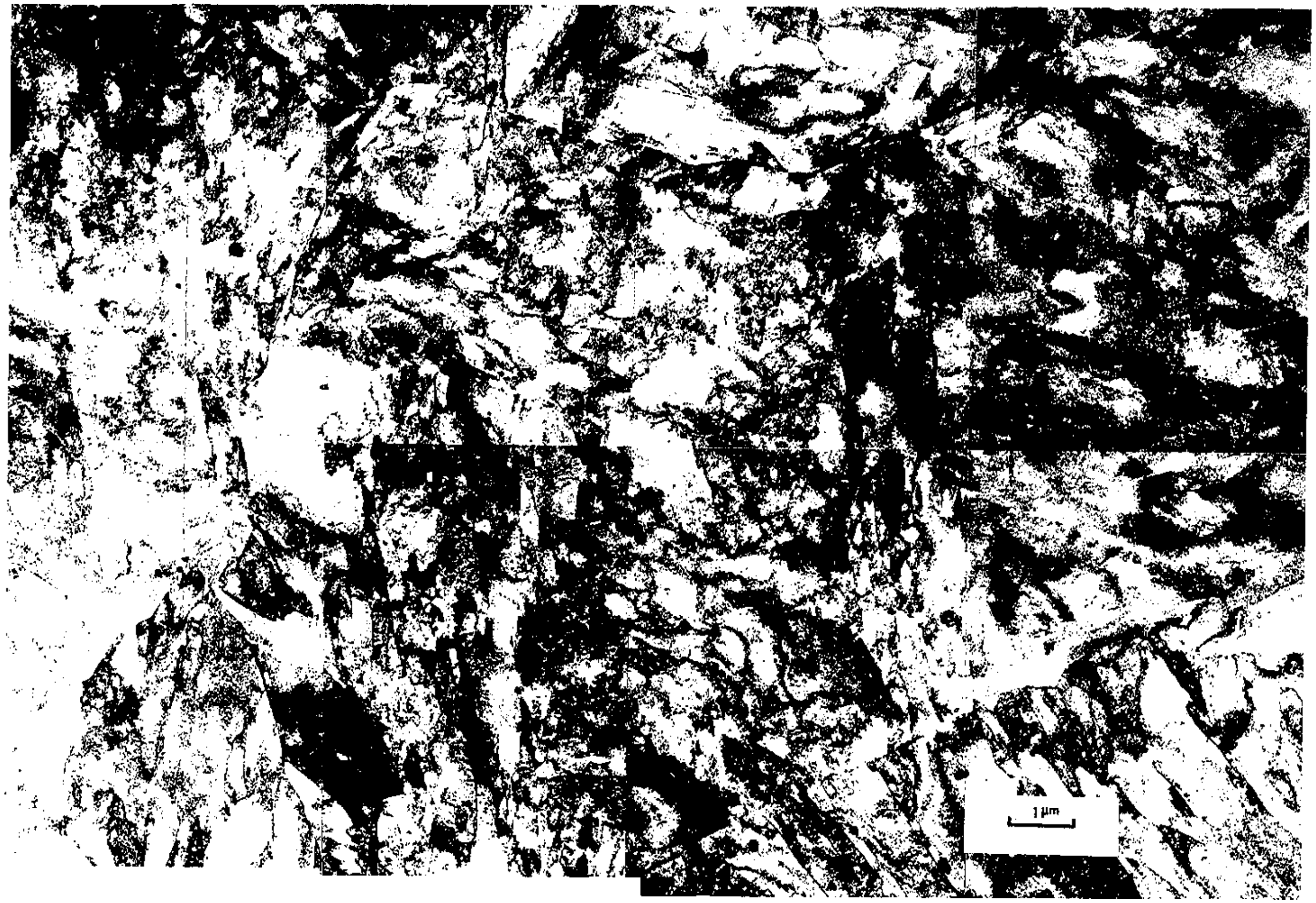
(i) Recrystallisation has occurred. The grain size is about 25 μm.

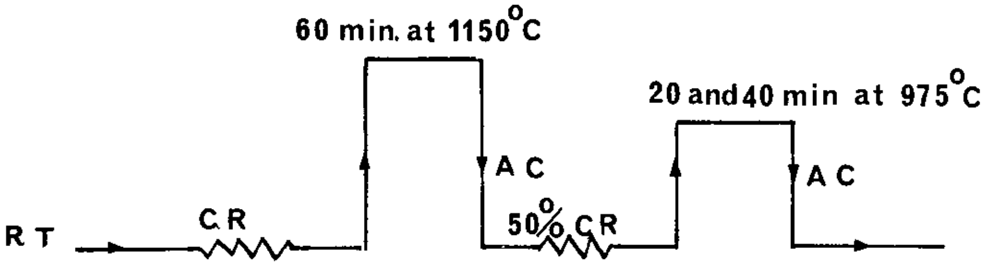
(ii) Type A precipitates are still observed.

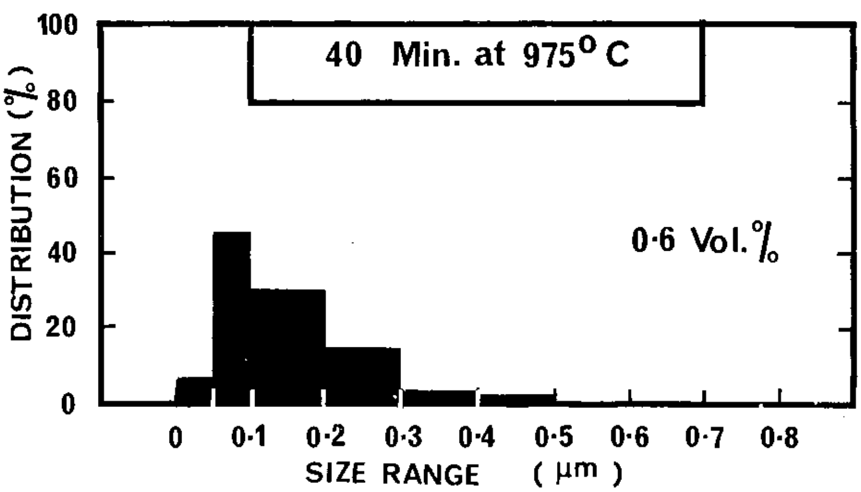
(iii) The volume of precipitates has decreased to ~ 0.5 per cent.

FIGURE 19. MAR 400, 20 MINUTES AT 975°C


1 µm


1 µm





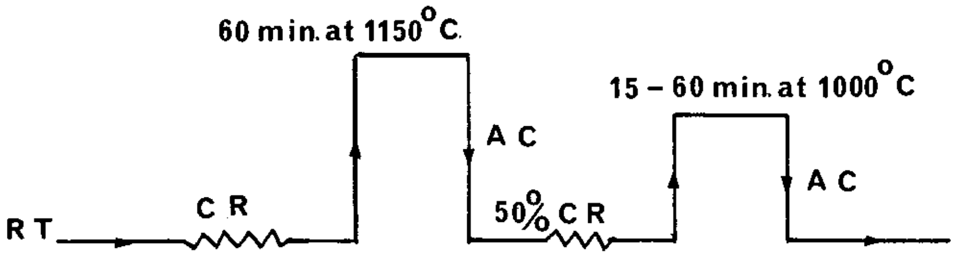
OBSERVATIONS

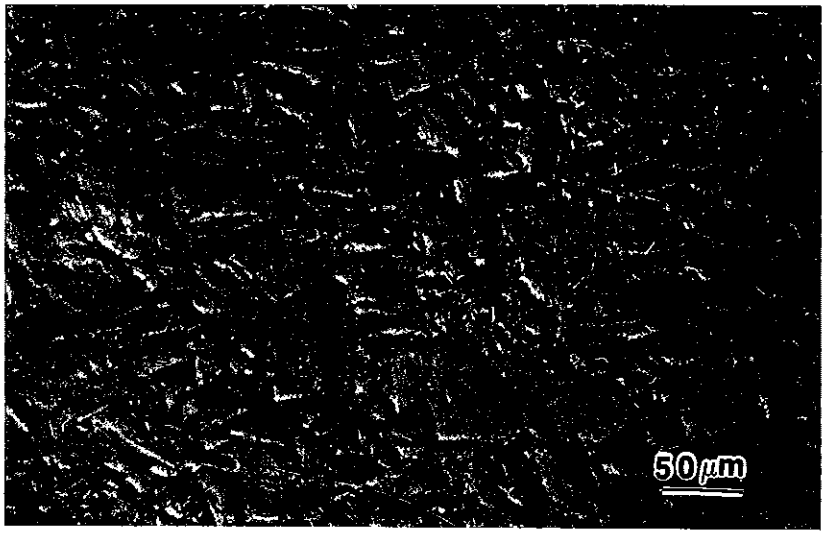
(i) No grain growth has occurred compared with 20 min. at 975°C. The average grain size is ~ 25 μm.

(ii) Undissolved type A precipitates are still noted.

(iii) The volume of precipitate, 0.6 per cent, is similar to that measured after 20 min. at 975°C.

FIGURE 20. MAR 400, 40 MINUTES AT 975°C





OBSERVATIONS

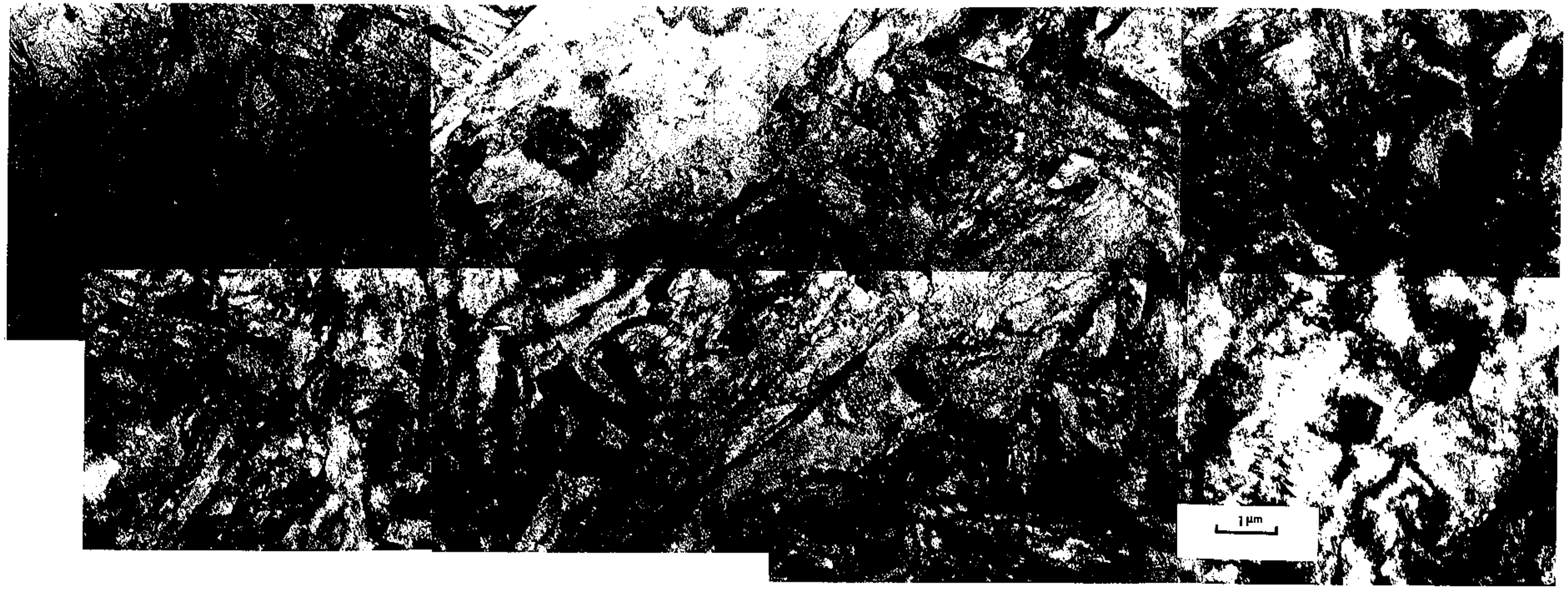
(i) Complete recrystallisation has occurred.

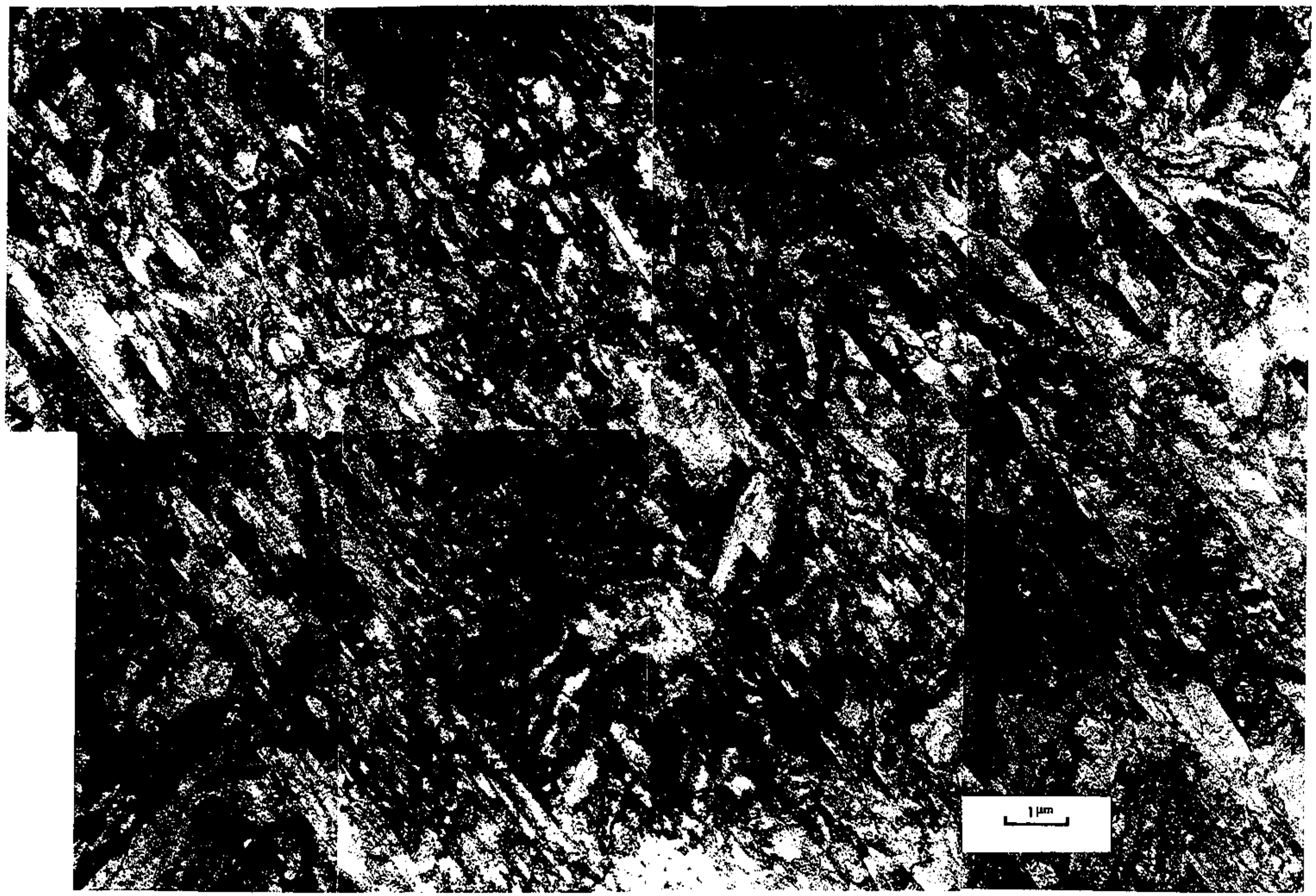
(ii) Grain size is approximately 35 µm.

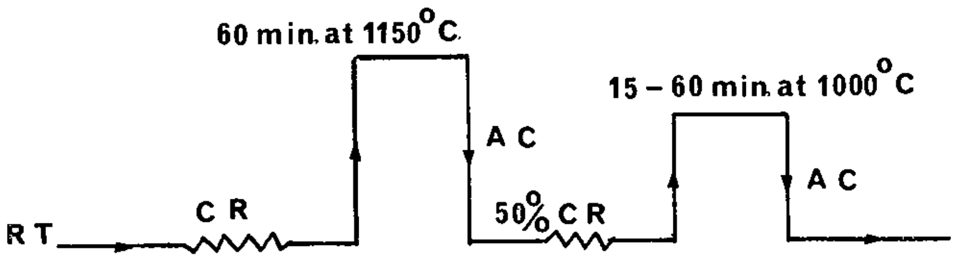
(iii) No precipitates are observed.

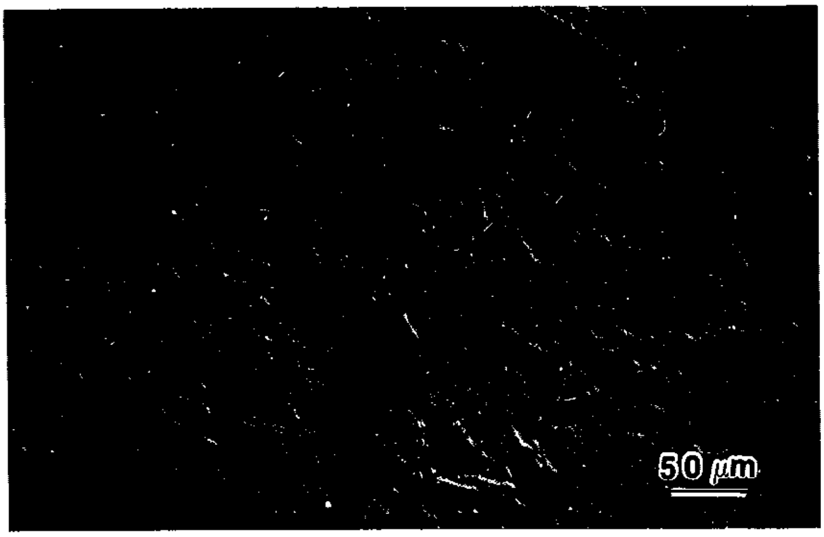
(iv) Some rolling deformation is noted.

FIGURE 21. MAR 400, 15 MINUTES AT 1000°C


1 µm


1 µm



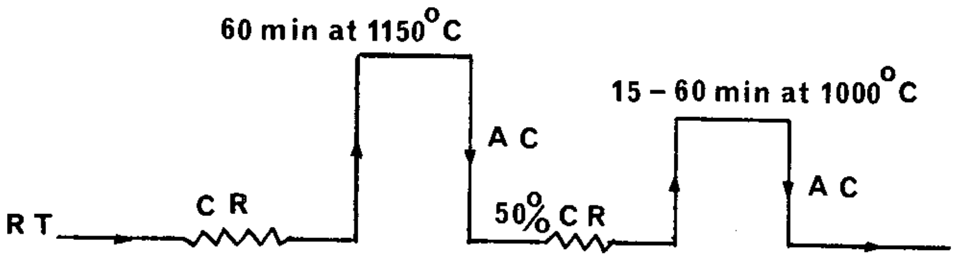


OBSERVATIONS

(i) A recrystallised grain size of approximately 50 μm is noted.

(ii) No precipitates are observed.

FIGURE 22. MAR 400, 30 MINUTES AT 1000°C

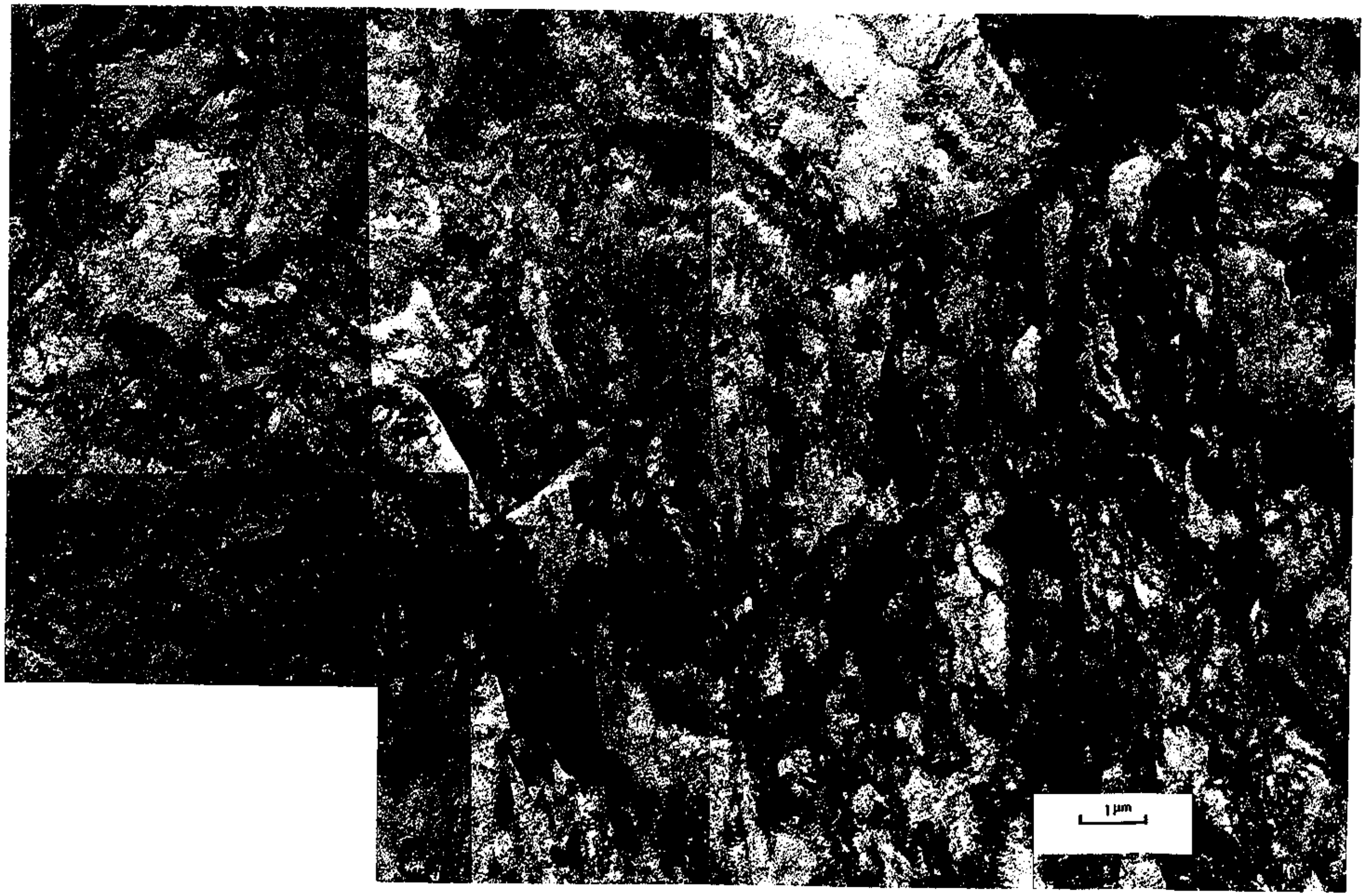


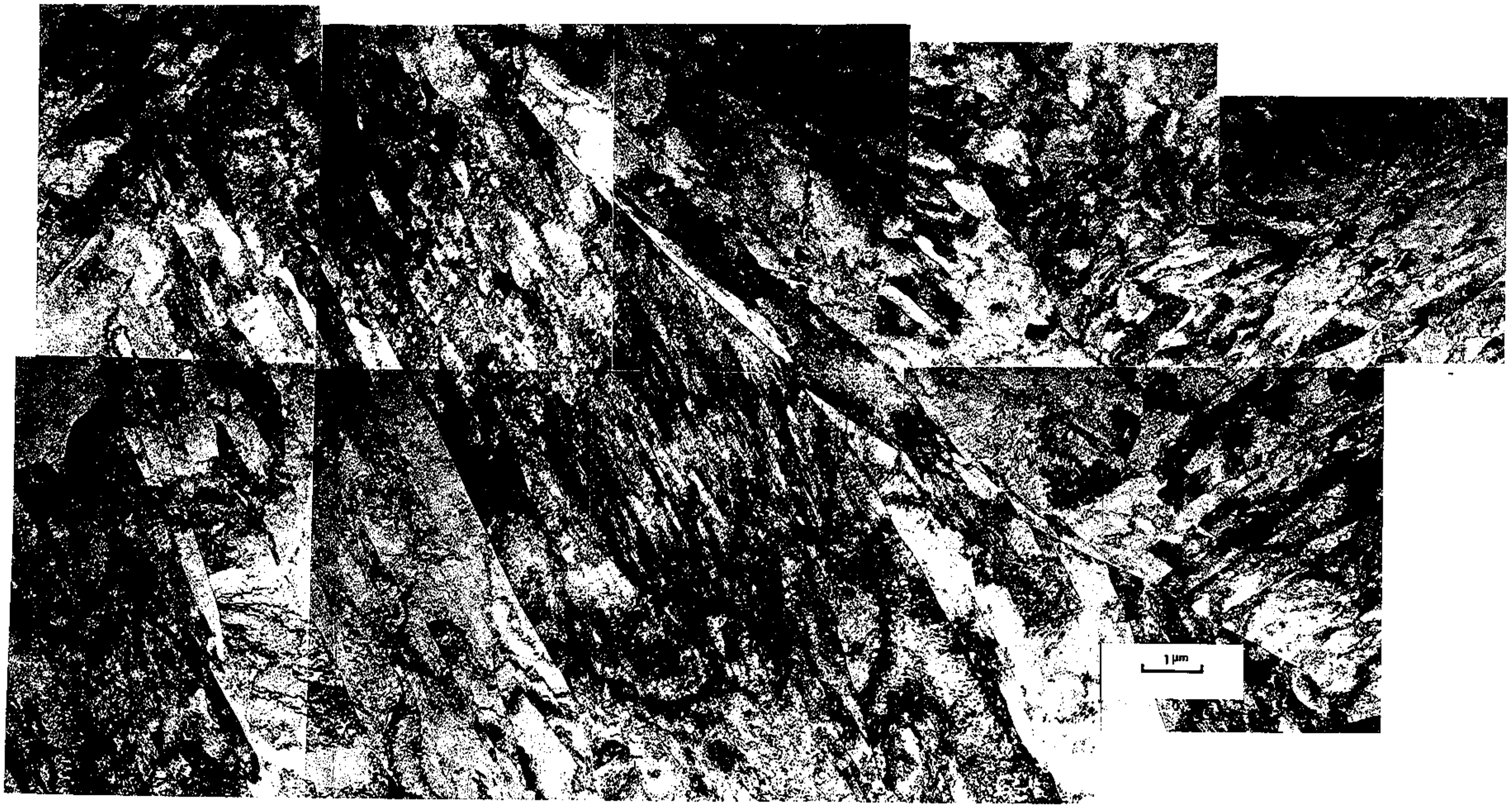
OBSERVATIONS

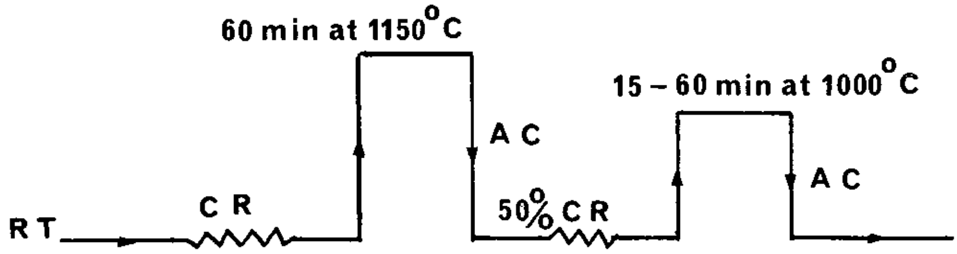
(i) The recrystallised grain size is ~ 75 µm.

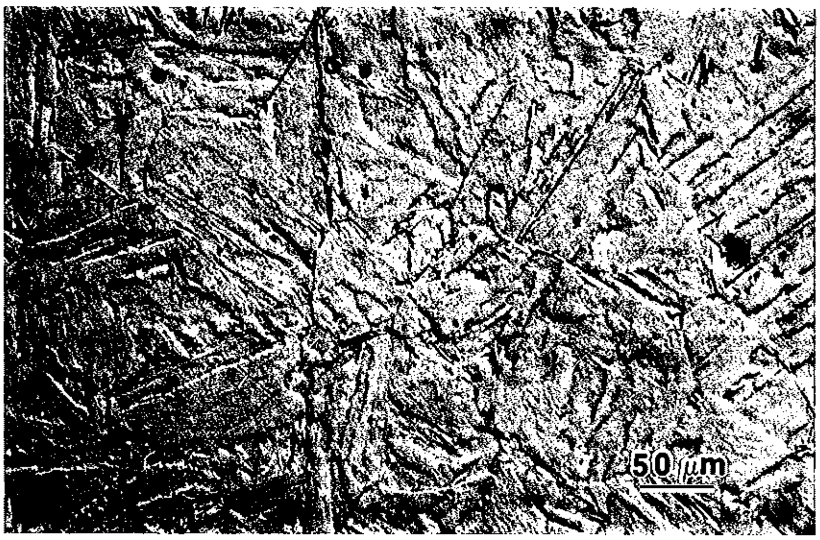
(ii) No precipitates are observed.

FIGURE 23. MAR 400, 45 MINUTES AT 1000°C


1 μm


1 µm





OBSERVATIONS

(i) A recrystallised grain size of ~ 125 μm is observed.

(ii) No precipitates are noted.

FIGURE 24. MAR 400, 60 MINUTES AT 1000°C

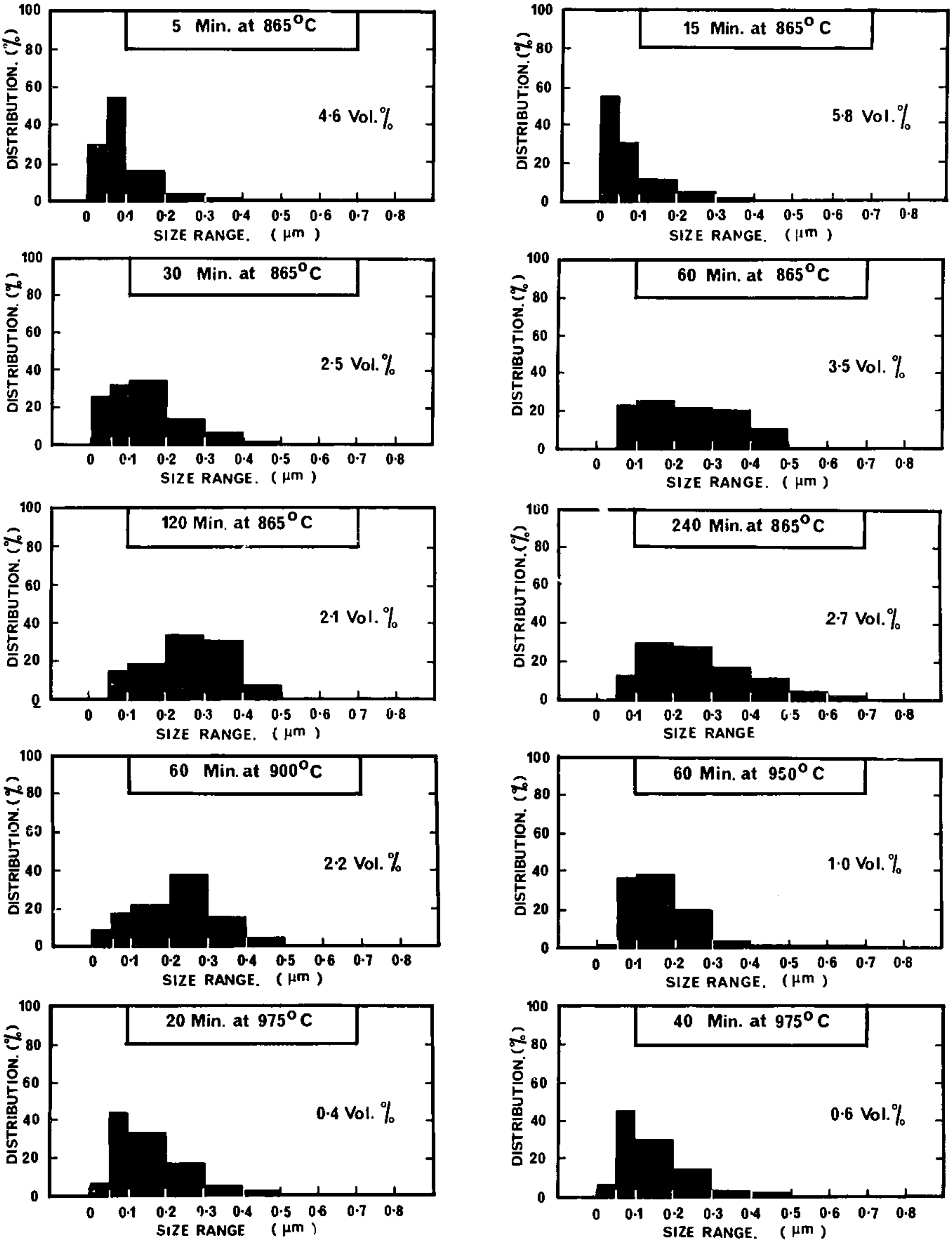


FIGURE 25. SIZE RANGE DISTRIBUTION OF PARTICLES OBSERVED IN MAR 400 SAMPLES

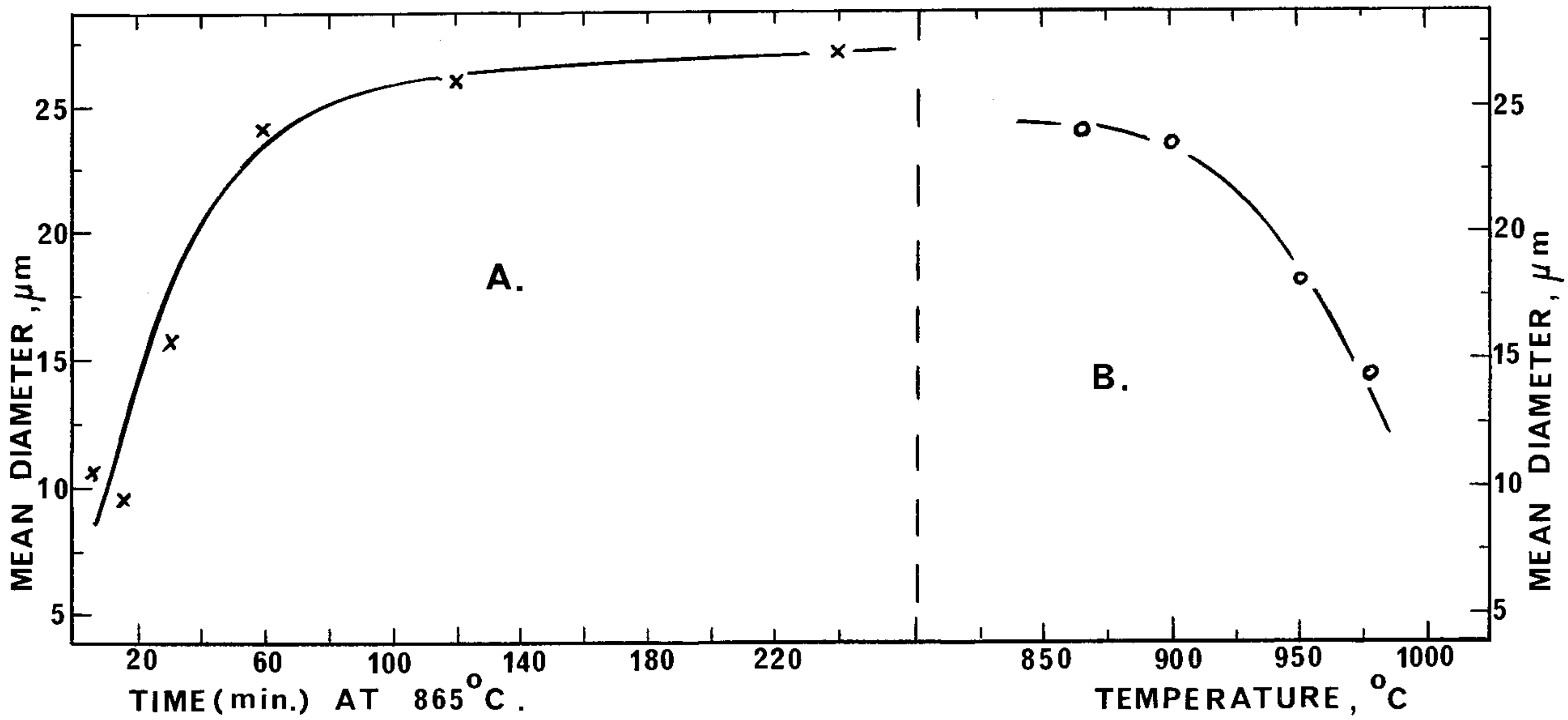


FIGURE 26. (A) MEAN PARTICLE DIAMETER VERSUS TIME AT 865°C
(B) MEAN PARTICLE DIAMETER VERSUS TEMPERATURE (60 MINUTES)

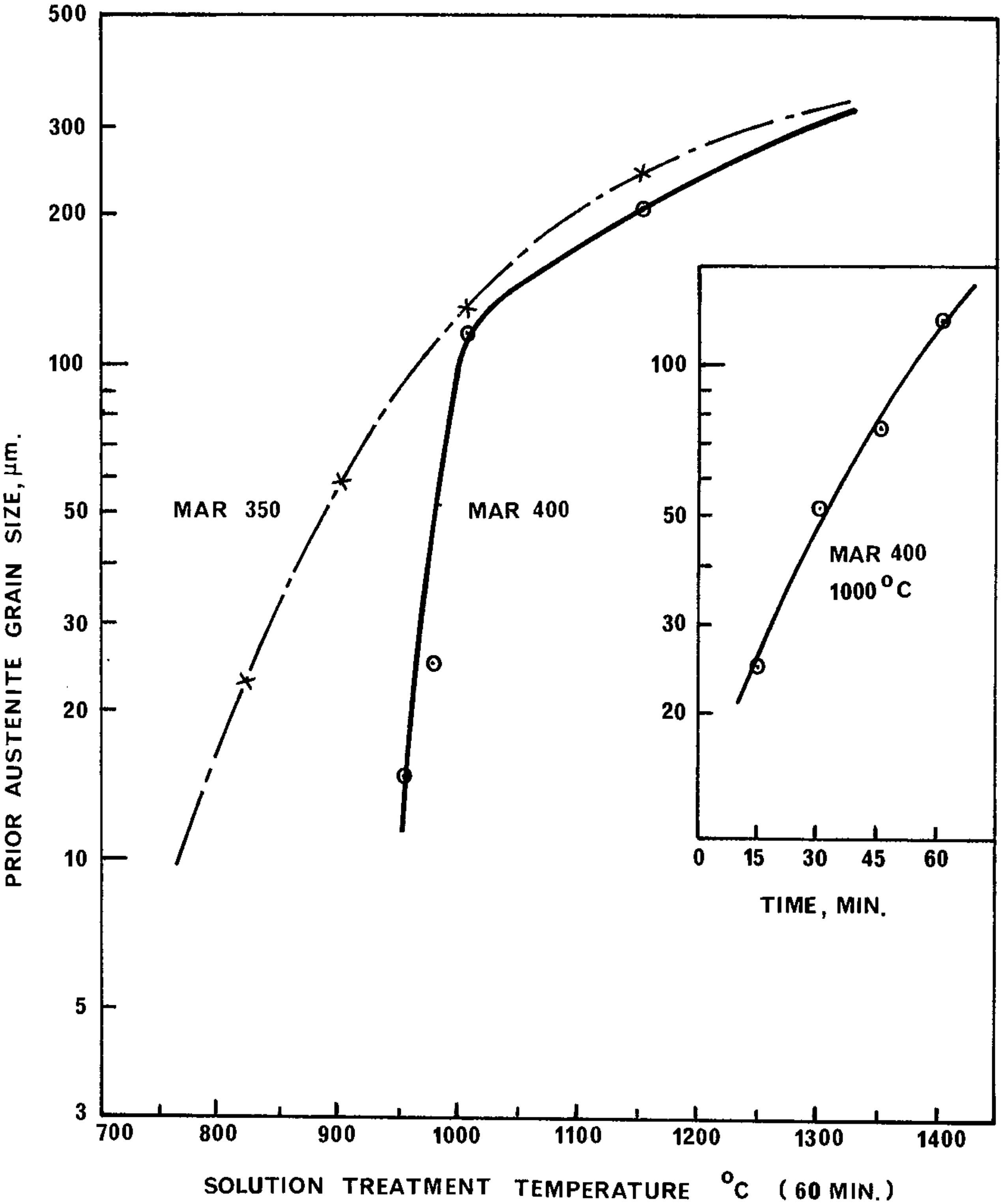


FIGURE 27. LOGARITHM OF RECRYSTALLISED GRAIN SIZE VERSUS SOLUTION TREATMENT TEMPERATURE.

INSET. LOGARITHM OF GRAIN SIZE FOR MAR 400 VERSUS TIME AT 1000°C

APPENDIX A

STRUCTURAL IDENTIFICATION OF PARTICLES

Structural identification of the particles labelled A in Figures 10 to 19 was carried out using electron diffraction. Figure A1 shows a typical particle (arrowed), the electron diffraction pattern obtained from it, and the interpretation of the pattern. The lattice spacings measured with this pattern are listed in Table A1. Comparison with the ASTM lattice spacings clearly identifies it as a μ-phase. The constitution of the μ-phase was determined using an energy dispersive X-ray analyser. Figure A2 shows the analyser traces obtained from a particle, the matrix, and the matrix trace stripped from the particle trace. Although the elemental components in the particle are primarily Mo and Fe, it is clear that a significant proportion of Co is present. A spurious peak due to chromium in the specimen chamber is present between the main Mo and Fe peaks. The composition of the μ-phase may be written as $(FeCo)_7Mo_6$.

The small size of the precipitate labelled B in Figures 11 to 14 made the in situ identification by electron diffraction impossible. Structural and chemical identification of the precipitate is under way using both extracted particles and specially heat-treated samples.

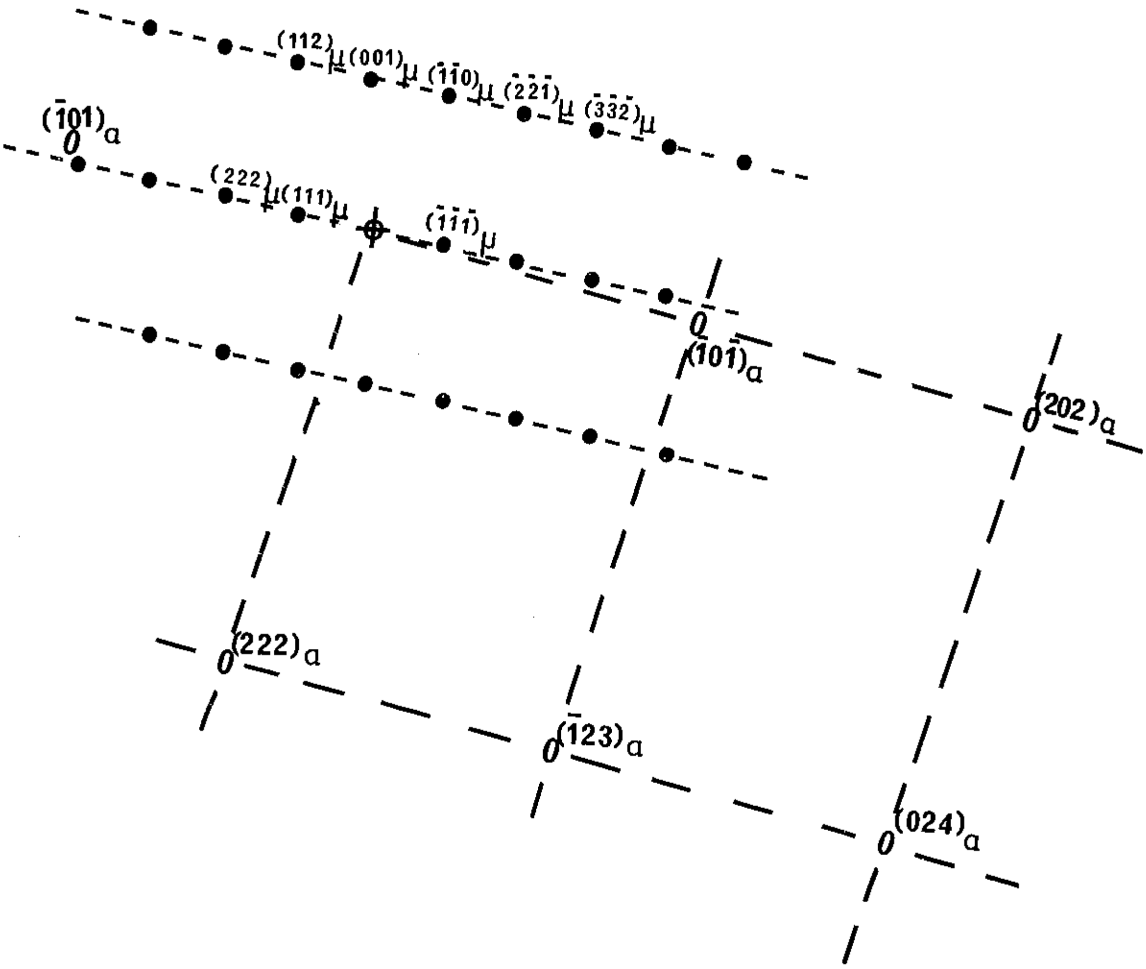
TABLE A1

LATTICE SPACINGS MEASURED FROM THE ELECTRON DIFFRACTION PATTERN IN FIGURE A2

(hkl)	ASTM Spacings for Co_7Mo_6 (nm)	Measured Lattice Spacings (nm)
(111)	0.855	0.852
(222)	0.427	0.427
(333)	0.285	0.284
(444)	0.2137	0.2135
($\bar{2}\bar{2}\bar{1}$)	0.3217	0.322
($\bar{1}\bar{1}0$)	0.3931	0.392
(001)	0.4078	0.4064
(112)	0.347	0.3455
(223)	0.274	0.2734
($\bar{1}\bar{1}1$)	0.2059	0.2065
($\bar{2}\bar{2}0$)	0.1966	0.196
(002)	0.2039	0.2032
(334)	0.21785	0.2159
($\bar{3}\bar{3}2$)	0.2532	0.2533

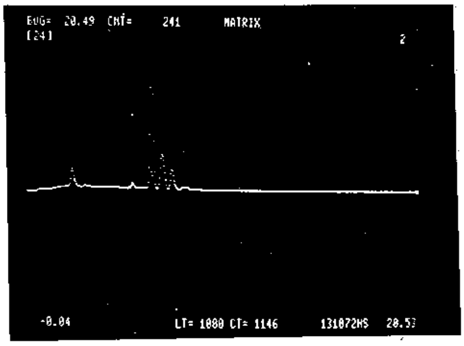
(a)

(b)

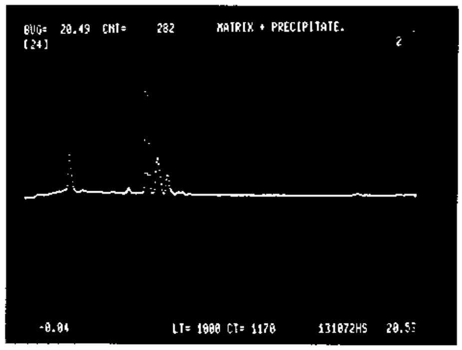


(c)

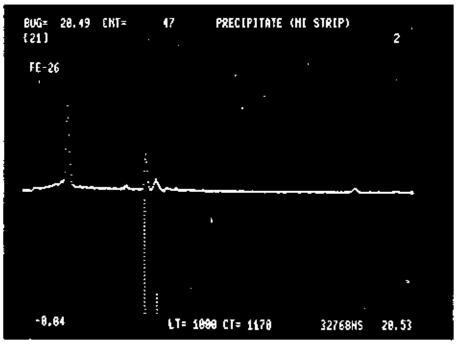
FIGURE A-1 (a) TEM OF THE MAR 400 SAMPLE AFTER SOLUTION TREATMENT AT 865°C FOR 60 MINUTES; (b) ELECTRON-DIFFRACTION PATTERN OBTAINED FROM THE ARROWED PARTICLE IN (a); AND (c) INTERPRETATION OF DIFFRACTION PATTERN $(hkl)_a$ - REFER TO THE Fe RICH MATRIX $(hkl)_\mu$ - REFER TO THE μ-PHASE



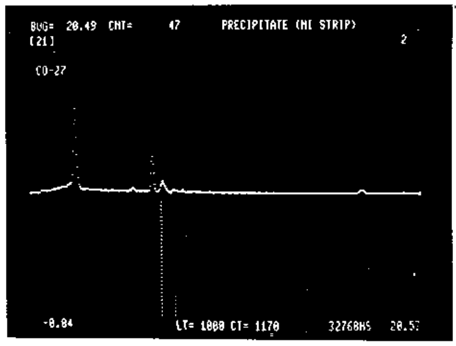
(a)



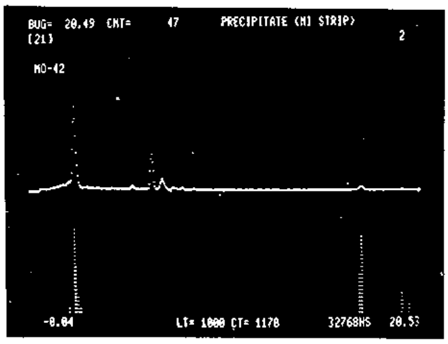
(b)



(ci)



(cii)



(ciii)

FIGURE A-2 ENERGY DISPERSIVE ANALYSER TRACES OBTAINED FROM (a) THE MATRIX; (b) THE MATRIX AND A LARGE μ-PHASE PARTICLE; AND (ci) TRACE (a) STRIPPED FROM TRACE (b) AND SHOWING Fe PEAK POSITIONS, (cii) TRACE (a) STRIPPED FROM TRACE (b) AND SHOWING Co PEAK POSITIONS, AND (ciii) TRACE (a) STRIPPED FROM TRACE (b) AND SHOWING Mo PEAK POSITIONS