

# High-temperature deformation of Fe<sub>3</sub>Al alloys with TiB<sub>2</sub> or Ce additions

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## Abstract

High-temperature tensile and creep properties represent a problem retarding the application of Fe<sub>3</sub>Al based intermetallics in technical practice. These properties can be improved by additives and/or by a combination of deformation and thermal treatment. The Fe-28Al-4Cr type intermetallics modified by TiB<sub>2</sub> (alloy A) or Ce (alloy B) additions were studied both in the as-received state and after annealing at 1150 °C for 2 hours. Tensile and creep properties were measured in the temperature range from 600 to 900 °C and explained on the basis of microstructural investigations.

**Key words:** iron aluminides, high temperature deformation, microstructure

## 1. Introduction

Ordered intermetallic alloys exhibit generally a good high-temperature strength, low density, and environmental resistance, and may be, therefore, potential materials for high-temperature applications. On the other hand, they are very brittle, have low toughness and are prone to grain boundary embrittlement, which results in their poor fabricability and machinability. The general problem of room temperature brittleness may be overcome in some intermetallics by a suitable thermal and mechanical treatment.

A very good corrosion, carburization and oxidation resistance at high temperatures is the reason for the increasing interest in these materials (see e.g. [1, 2]). However, it is necessary to improve further their high-temperature tensile and creep strength. Very recently Morris et al. [3, 4] have summarized the results of high-temperature deformation experiments performed at some Fe<sub>3</sub>Al-based intermetallics. It was shown that the most effective way to improve the high-temperature strength was the formation of particles that remained stable at high temperatures.

The typical representatives of such materials are Fe-28Al-4Cr intermetallics alloyed either by dissoluble

(up to 1150 °C) TiB<sub>2</sub> particles or by Ce supporting the formation of mixed (Cr, Fe) carbides [5]. It is the purpose of this paper to present data on high temperature deformation behaviour of these intermetallics obtained both from tensile tests and creep experiments and to compare the efficiency of both additions. Special attention is paid to the influence of thermal treatment of both materials on their mechanical properties.

## 2. Experimental procedure

Two alloys, whose compositions in at.% are given in Table 1, were investigated. The alloys were melted in a vacuum furnace and cast in argon atmosphere at the Research Institute of Metals, Ltd., Panenské Břežany, Czech Republic.

Alloy A was cast as an ingot of 137 mm in diameter. This was hot extruded at 1140 °C at an area ratio of 12 : 1 (reduction 92 %) into the shape of tube with 8 mm thick wall. The tube was left to cool down to the room temperature in a period of 4 h. Tensile and creep specimens were cut parallel to the extrusion direction with the gauge length of 48 mm and diameter of 4 mm.

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Table 1. Chemical compositions of materials (at.%)

	Al	Cr	TiB <sub>2</sub>	Ce	C	Fe
Alloy A	30.2	3.9	2.84		0.16	balance
Alloy B	28.0	4.1		0.02	0.16	balance

Alloy B was cast as a slab 120 × 40 mm which was hot rolled at 1200 °C in several steps to a sheet 13 mm thick. The total reduction was 68 %. The sheet was quickly cooled in oil. The tensile and creep samples with the gauge length of 25 mm and diameter of 5 mm were machined parallel to the rolling direction.

Two sets of samples of alloys A and B were investigated. The first one was in the as-received state after hot extrusion or hot rolling, the second one was thermally treated (TT) – annealed at 1150 °C for 2 hours in air and then cooled slowly outside the furnace.

Tensile tests of the alloy A were performed in an air furnace at temperatures between 600 and 900 °C using a constant crosshead velocity corresponding to the initial strain rate of  $1.8 \times 10^{-3} \text{ s}^{-1}$ . The temperature differences along the gauge length remained under 5 K even at the highest testing temperature. The strain rate change method was used for the evaluation of the strain rate sensitivity of the tensile stress. Tensile tests in the alloy B were performed at the strain rates of  $10^{-4}$  and  $10^{-2} \text{ s}^{-1}$  and the data corresponding to the strain rate  $10^{-3} \text{ s}^{-1}$  necessary for the comparison with the alloy A were obtained by an extrapolation assuming the relation between the tensile stress  $\sigma$  and strain rate  $\dot{\epsilon}$  in the form

$$\sigma = K_1 \dot{\epsilon}^m, \quad (1)$$

where  $K_1$  is a constant and  $m$  is the strain rate sensitivity parameter.

Creep tests were performed at constant loads at temperatures of 600 and 700 °C in air. The values of time to rupture (TTR) and minimum creep rate (MCR) were evaluated from these experiments as a function of load. The stress sensitivity of the creep rate was evaluated from individual experiments performed at different loads according to the formula

$$\dot{\epsilon} = K_2 \sigma^n, \quad (2)$$

where  $K_2$  is a constant and  $n$  is the stress sensitivity exponent.

The microstructure was studied using both light optical (LOM) and transmission electron microscopy (TEM) on a plane perpendicular to the extrusion or rolling direction. The samples for LOM were polished using Struers OP-S solution, etched using Rollason solution (100 ml H<sub>2</sub>O + 50 ml HCl 38 % + 5 g Fe<sub>3</sub>Cl)

and observed in Nikon Epiphot 200 microscope. Thin foils for TEM were prepared by electropolishing in 20 % solution of HNO<sub>3</sub> in methanol at –30 °C and studied using JEOL 2000 FX transmission electron microscope.

### 3. Experimental results

The true stress vs. strain curves of the alloy A (both in the as-received and annealed state) are given in Fig. 1 for various deformation temperatures. All curves exhibit a strain-softening region the length of which increases with increasing temperature. The initial region of strain hardening is observed only at temperatures 600 and 700 °C and becomes nearly negligible at both higher temperatures of 800 and 900 °C. Figure 2 shows the comparison of the 0.2 % offset yield stresses for both alloys and documents that the addition of TiB<sub>2</sub> results in a higher strength in comparison with the alloy B modified by Ce. Thermal treatment enhances slightly the yield stress of the alloy A. The same influence of alloying and thermal treatment was observed for the ultimate tensile strength.

Remarkably high values of ductility over 100 % were found at temperatures above 700 °C for the as-extruded alloy A (Table 2). These values are close to the bottom limit of superplasticity. Thermal treatment reduces ductility significantly. High values of ductility are usually accompanied by an enhanced strain rate sensitivity of the flow stress. The strain rate sensitivity parameter  $m$  values are also summarized in Table 2. Maximum values close to 0.3 were found at temperatures above 700 °C in the as-extruded alloy A, thermal treatment reduces these high parameter  $m$  values. A good correlation between ductility and parameter  $m$  may be seen.

Previous experiments confirmed a positive influence of thermal treatment on creep characteristics of

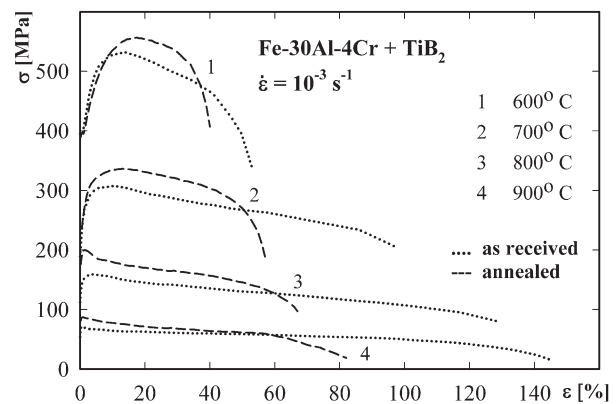


Fig. 1. True stress vs. strain curves for the alloy A.

Table 2. Ductility  $A$  and strain rate sensitivity parameter  $m$  of the alloy A modified by  $TiB_2$

Material A	$T$ (°C)	600	700	800	900
Non-treated	$A$ (%)	55	104	140	150
	$m$	0.12	0.21	0.27	0.29
Thermally treated	$A$ (%)	40	57	67	82
	$m$	0.12	0.14		0.18

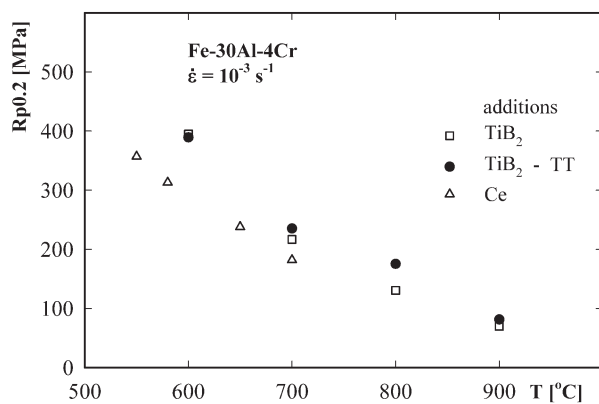


Fig. 2. The influence of deformation temperature on the yield stress of the A and B alloys.

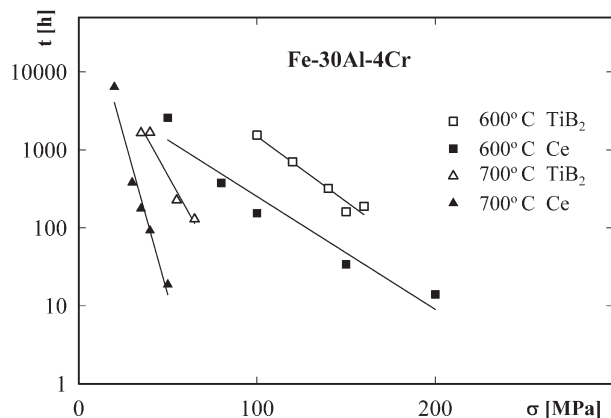


Fig. 3. The influence of stress on the time to rupture (TTR) of the annealed A and B alloys.

the alloy B – higher TTR values and lower MCR values were found in the thermally treated material at all loads used [6]. Figure 3 compares the TTR values found in both alloys after thermal treatment. Substantially higher TTR values were observed in alloy A at all loads and both temperatures used. Figure 4 documents significantly lower MCR values in alloy A. All experiments document a good correlation between both creep characteristics – the increase of TTR is always accompanied by a decrease in MCR.

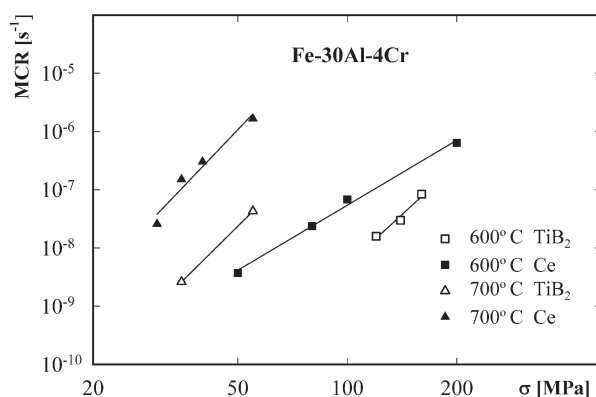


Fig. 4. The influence of stress on the minimum creep rate (MCR) of the annealed A and B alloys.

Table 3. The influence of creep temperature  $T$  on the stress exponent  $n$  for different alloys

$T$ (°C)	500	600	700	800	900
Alloy A – thermally treated		6.2	6.2		
Alloy B – not treated	5.9	4.3	4.1	4.0	3.9
Alloy B – thermally treated	7.0	4.0	6.5		

The stress exponent  $n$  was determined from the dependence of MCR on load and its values are summarized in Table 3.

Despite of a strange value for the thermally treated alloy B at 600°C it can be concluded that the exponent  $n$  values are similar for both thermally treated alloys, slightly lower values were found in the non-treated alloy B. A comparison of the parameter  $m$  and stress exponent  $n$  values measured in the thermally treated alloy A at temperatures 600 and 700°C ( $m$  about 0.13 and  $n$  over 6) shows a relatively good agreement with the relation  $n = 1/m$  following from the definition of both parameters.

In order to explain the deformation characteristics of both alloys their microstructure was investigated especially from the point of view of their phase composition. Alloy A contains already in the non-treated state relatively large volume fraction of  $TiB_2$  particles arranged in rows parallel to the extrusion direction (Fig. 5). The particles have the shape of needles with a hexagonal cross-section (Fig. 6). The dimensions of needles exhibit a broad distribution – e.g. their length varies from 5–10  $\mu m$  in Fig. 5 down to 500 nm in Fig. 6a. These particles do not dissolve during thermal treatment at 1150°C.

A different phase composition was observed in alloy B. The microstructure of samples crept at 600°C is documented in Fig. 7. The as-received material contains only sporadic particles of the size up to 200 nm

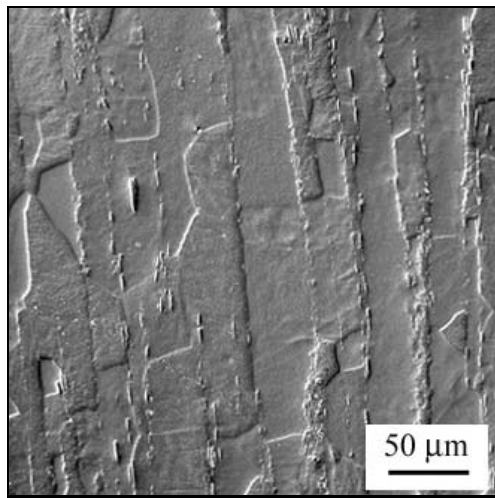


Fig. 5. The microstructure of the not annealed alloy A, the needles are arranged parallel to the extrusion direction.

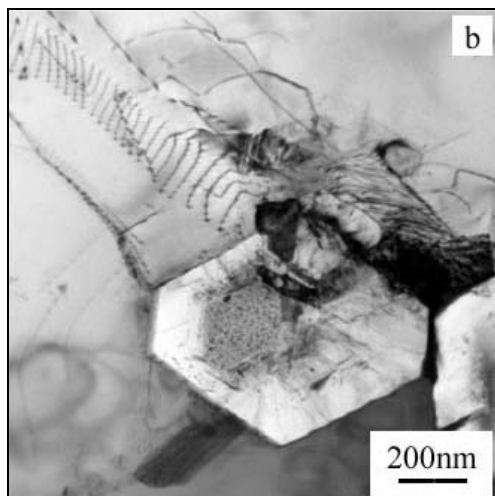
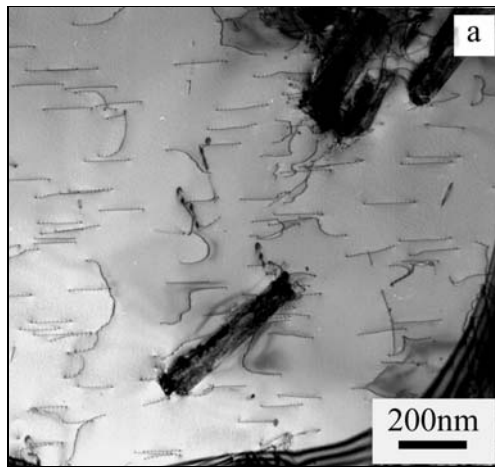


Fig. 6. The microstructure of the alloy A after creep at 600°C, (a) parallel to the rolling direction, (b) perpendicular to the rolling direction.

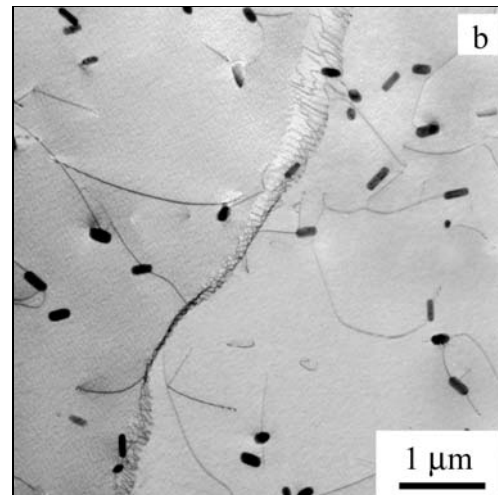
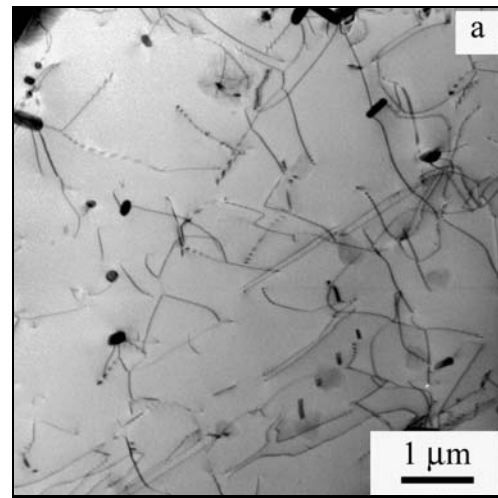


Fig. 7. Microstructure of the alloy B after creep at 600°C, (a) initial state not annealed, (b) initial state annealed 1150°C/2 hours.

that interact with lattice dislocations (Fig. 7a). The volume fraction of these particles is much higher in the annealed material (Fig. 7b). The precipitates were identified as Cr-Fe-C carbide particles with hexagonal crystal lattice containing carbon between 15 and 30 at.% [5].

#### 4. Discussion

The grain and dislocation structure of the as-extruded alloy A after deformation in tension at high temperatures was described in [7]. Dynamic recovery was observed at deformation temperatures below 800°C, dynamic recrystallization occurred at 900°C. These conclusions resulted from the microstructure investigation using both LOM and TEM and were supported by the measurement of grain aspect ratio. A very similar development of grain and boundary struc-

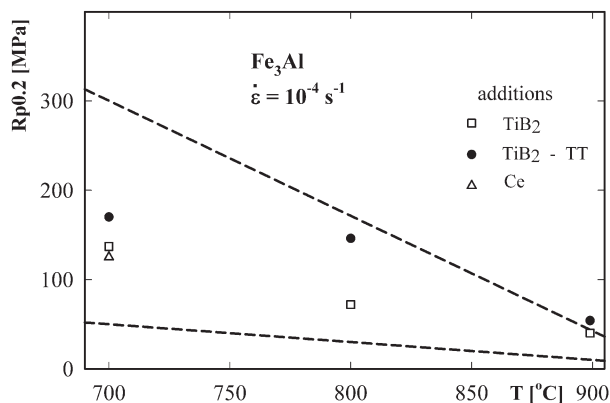


Fig. 8. The comparison of the yield stress values for alloys A and B with data presented by Morris et al. [4] (the region between dashed lines).

ture was found in the annealed alloy A as well. The shape of stress-strain curves, especially the absence of remarkable strain hardening correlates well with the operation of restoration processes mentioned.

The high temperature yield strength of our materials is compared in Fig. 8 with the data on  $\text{Fe}_3\text{Al}$  based alloys reported and summarized by Morris et al. [4]. Two dashed lines in Fig. 8 are the limits of the area that includes all previously published data taken from [4]. Our data are close to the center of this region for 700°C, nevertheless they shift to the top of this region with increasing deformation temperature. This comparison documents clearly that our materials belong to the best materials with respect to their high temperature stability.

The main aim of the present experiments was to improve high-temperature mechanical properties of two types of  $\text{Fe}_3\text{Al}$  alloys by a thermal treatment. McKamey and Masiasz [8] reported the best creep properties of  $\text{Fe}_3\text{Al}$ -type intermetallics in Fe-28Al-5Cr alloyed mainly by Nb and Mo. A decrease of MCR and an increase of TTR and creep strength resulting from a high temperature annealing at 1150°C were explained by combined effects of solid solution hardening and/or precipitation strengthening by Mo and Nb containing particles. A similar explanation can be also used for the interpretation of our results.

In order to understand the positive effect of high temperature annealing the precipitation processes were studied in alloy B [5]. Figure 9 shows that precipitates (Cr-Fe-C carbide particles) are formed in this alloy during annealing at temperatures between 500 and 900°C, and annealing at higher temperatures results in their dissolution. These precipitates probably hinder the movement of dislocations and thus improve creep and tensile properties. The main difference between the as-received and annealed samples of the alloy B can be found in the rate of their cooling from high temperatures. The last step in the preparation of the

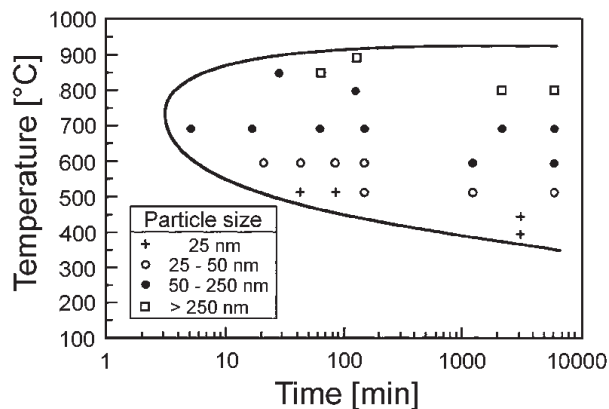


Fig. 9. TTT diagram of the alloy B documents the presence of carbide particles (according to [5]).

alloy B was hot rolling at 1200°C followed by rapid cooling into oil. The formation of precipitates is suppressed since the sample does not enter the “precipitation nose” during cooling. Therefore, the as-received material should not generally contain any carbide particles. Some particles present in the material crept at 600°C (Fig. 7a) were probably formed during this high-temperature deformation. On the other hand, the annealed material was cooled slowly from the temperature of 1150°C. During this slow cooling, the sample enters the “precipitation nose” and numerous precipitates are formed. The volume fraction of these precipitates is therefore higher than that in the not-annealed material (Fig. 7b).

It is the main task for future to prepare materials containing particles that would be stable at even higher temperatures. Alloy A represents the first step to the solution of this problem. The structure we got using hot extrusion contains relatively large volume fraction of  $\text{TiB}_2$  needles. No quantitative measurement of the volume fraction of  $\text{TiB}_2$  needles was performed nevertheless the qualitative comparison of the microstructure in the as-received state and after annealing at 1150°C did not show any important difference. Alloy A can be thus considered as a composite material with a stable volume fraction of  $\text{TiB}_2$  needles. Two problems remain to be explained:

- the absence of carbide particles in the annealed material A
- the reason for the improvement of strength characteristics due to annealing at 1150°C.

Figure 6 shows that the alloy A does not contain larger carbide particles even after exposure to the temperature of 600°C where a massive precipitation occurred in the alloy B (this difference supports the idea that Ce initiates the carbide precipitation). Nevertheless, the changes in deformation characteristics of alloy A due to annealing at 1150°C suggest some changes in its phase composition. Large val-

ues of ductility and strain rate sensitivity, simultaneously with the occurrence of transition phenomena after strain rate changes were interpreted as a result of the viscous glide of lattice dislocations [7]. This deformation mechanism assumes the presence of mobile solutes. On the other hand, lower values of ductility and strain rate sensitivity are usually observed in precipitation or dispersion strengthened materials. Both these effects were observed in the alloy A annealed at 1150°C and yield thus an indirect evidence for some precipitation process occurring during annealing. Very recent experiments performed on the Zr containing Fe<sub>3</sub>Al-based intermetallics revealed a similar absence of larger carbide particles even after annealing at high temperatures [9]. However, a detailed TEM investigation of this material confirmed the presence of very fine carbide particles at some places. Since the distribution of these particles was extremely inhomogeneous many of TEM micrographs did not contain any particles. These results stimulated us to re-analyse the microstructure of the alloy A. The TEM micrograph in Fig. 10 taken at a large magnification really confirms the presence of very small and inhomogeneously distributed coherent particles in the alloy A annealed at 700°C for 10 hours.

## 5. Conclusions

Two simply alloyed Fe<sub>28</sub>Al<sub>4</sub>Cr-type aluminides were tested for high temperature applications. TiB<sub>2</sub> and Ce were used as additives. The effect of annealing at 1150°C/2 hours on high-temperature tensile and creep tests was investigated. The experimental results can be summarized as follows:

a) The high-temperature strength is always higher for annealed material.

b) The high temperature deformation characteristics are better for the TiB<sub>2</sub> containing alloy than for that containing Ce. This is valid for both tensile and creep tests.

c) The precipitation hardening (chromium-iron carbide) is responsible for the strengthening of Ce containing alloy.

d) The TiB<sub>2</sub> containing alloy can be considered as a composite material with a stable volume fraction of TiB<sub>2</sub> needles up to very high temperatures. The precipitation of very small coherent carbides occurs very inhomogeneously.

e) The data obtained are comparable to those referred by Morris [4]. The yield strength of the TiB<sub>2</sub> containing alloy observed at 900°C belongs to the best values reported.

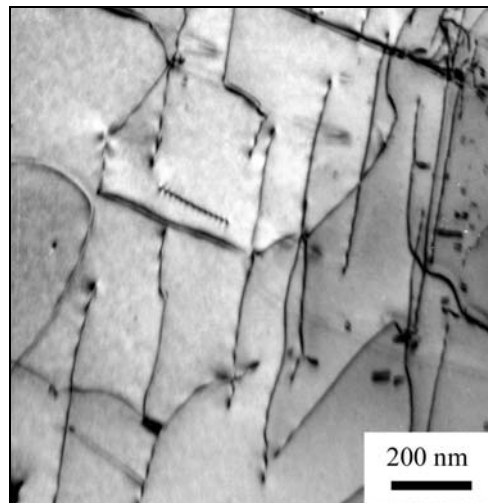


Fig. 10. Microstructure of the alloy A annealed at 700°C for 10 hours, coherent particles are inhomogeneously distributed.

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