

The effect of carbon on the structure of Fe-40Al- x C (at.%) ternary alloys

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Abstract

The phase composition of Fe-40Al- x C (at.%) alloys depends on the content of C. The part of the quasibinary phase diagram is determined using light optical microscopy (LOM), Vickers hardness measurements (HV) and X-rays diffraction (XRD). The composition of the tested alloys approaches in successive steps Pyroferal[®] alloy used in the fifties to replace the high chromium and nickel alloyed cast iron. The structural data are compared with those resulting from quasibinary Fe40Al- x C as well as ternary Fe-Al-C phase diagrams.

Key words: iron aluminide (Fe-Al type), phase composition

1. Introduction

Special properties of Fe-40Al (at.%) intermetallics (low density, oxidation and sulfidation resistance) enable their use for high temperature (HT) applications [1]. The typical cases of applications are porous filters for high sulphur contaminated gases, e.g. heat exchangers in gas turbines, protecting sheets in vessels, tubes in power stations, incinerators, structural components in furnaces, etc. Carbon in the FeAl (B2) iron aluminide is used e.g. to enhance the mechanical properties and to improve machinability.

The following phases exist near the composition Fe-40Al (at.%) in the ternary Fe-Al-C system depending on content of C and temperature:

- solid solution of C in B2 lattice
- graphite (G)
- carbide Fe₃AlC_{0.5} (perovskite), so called κ -phase (κ).

The presence of Si (~ 1 at.%) may initiate the formation of aluminium carbide Al₄C₃.

A very complex study of the phase composition of alloys based on FeAl aluminide was performed by Vyklický and Tůma [2] who also determined pseudobinary phase diagrams for different contents of Al. That one corresponding to 40 at.% Al is shown in Fig. 1. This

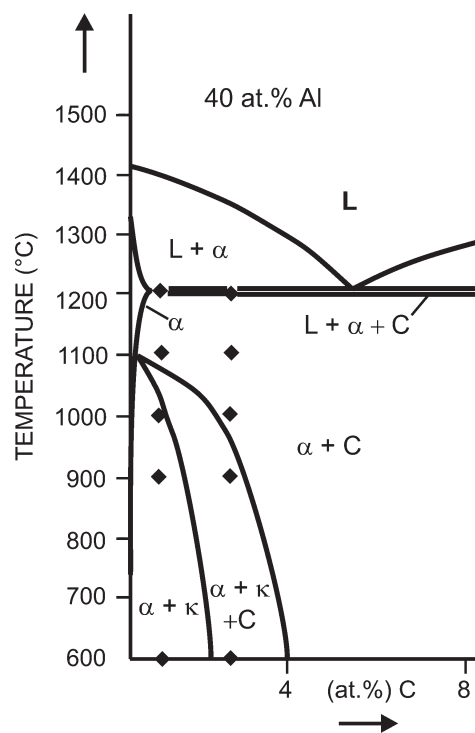


Fig. 1. Quasibinary diagram of Fe-40at.%Al-C according to data in [2].

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is the base material from which one can derive the series of alloys ending by Pyroferal[®] (ČSN 422484). Its composition is as follows: 44.4–46.5 at.% Al, 3.4–4.0 at.% C and max 0.5 at.% Mn, max 0.7 at.% Si. Maximum content of S, P is given by standard.

The mentioned Pyroferal[®] has a high resistance against thermal cycling, excellent resistance against chemical environments and also against abrasive wear. These properties enable to increase operating life time when compared to materials used before (Fe-Ni-Cr alloys). The reasons for favourable properties of Pyroferal[®] have never been fully understood and explained on the basis of structure (phase composition).

The aim of the present paper is to describe the structure of Fe-40Al (at.%) alloys with the increasing content of C. These results are used elsewhere to understand the mechanical properties at 600 °C [3].

2. Experimental technique

The nominal chemical compositions of alloy used for the experiment are summarized in Table 1. The alloys D-F were prepared by vacuum melting (10^{-1} – 10^{-2} mbar). The induction furnace Leybold was used. The slabs (cross section 20×32 – 35 mm) were rolled at 1200 °C to 8×35 – 40 mm using 8–15 % reductions. After each reduction the slab was heated in the furnace to 1280 °C.

Alloy H was prepared by sand casting.

Light optical microscopy (LOM), X-rays diffraction (XRD) and measurements of Vickers hardness (HV) were used to determine the phase composition of studied alloys. The phase structure, incl. grain boundaries was made visible using etching by emulsion OP-S (Struers). Also Nomarski contrast was applied to increase the resolution of phases. HV was measured using MICROMET 2100 – Buehler with image analyser. For XRD the system XRD7-FPM-Seifert was used.

Transmission electron microscopy (TEM) combined with the selected area diffraction (SAD) was used to identify the phases. The corresponding apparatus was JEOL FX2000. Phases were also identified by electron microanalysis.

3. Results

3.1. Structure of the alloy FA0.1C (D)

The size of equiaxed grains in the original material (after rolling at 1200 °C and free cooling) is larger than 500 μm . Only the B2 matrix without any other particles was identified (see Fig. 2) either inside the grains or along the grain boundaries. Carbon is fully soluble in the matrix. The average value of microhardness is 386 HV 0.05. The phase composition changed

Table 1. Composition of the alloys (at./wt.%)

Alloy	Denoted	Al	C	Si
FA0.1C	D	41.05/25.2	0.07/0.02	
FA0.8C	E	40.5/24.9	0.75/0.19	
FA1.7C	F	40.05/24.8	1.7/0.44	
FA1.9C	H	41.3/26.08	1.9/0.52	1.2/0.8

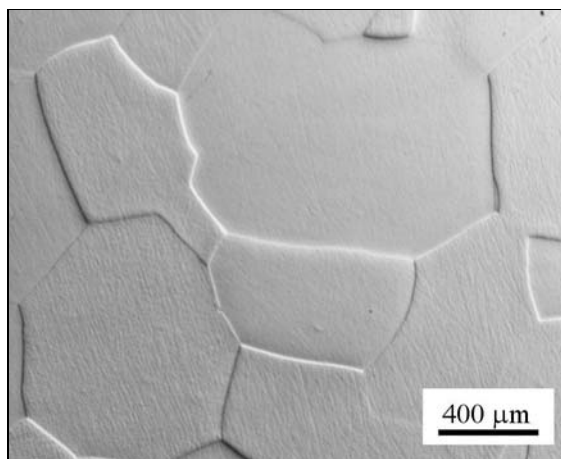


Fig. 2. Structure of alloy D, original state.

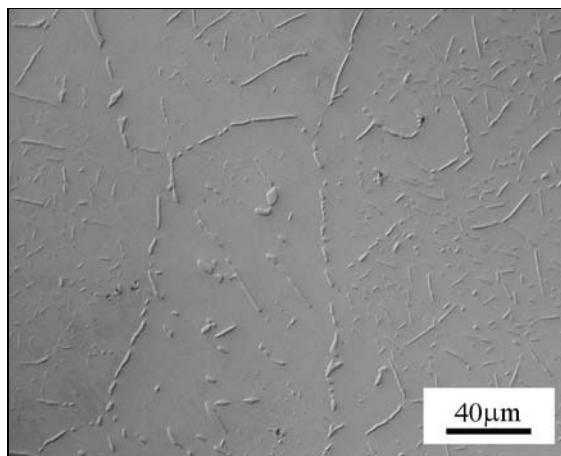


Fig. 3. κ -carbide in alloy E, original state.

neither after 1100 °C/8 h nor after 600 °C/100 h annealing.

3.2. Structure of alloy FA0.8C (E)

The original state: brighter rod-like particles are seen on the background situated along the grain boundaries and in the grains (Fig. 3). The values of

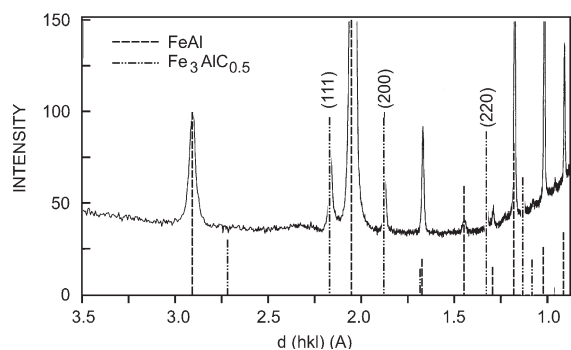


Fig. 4. XRD curve for sample E (annealed 600°C/100 h).

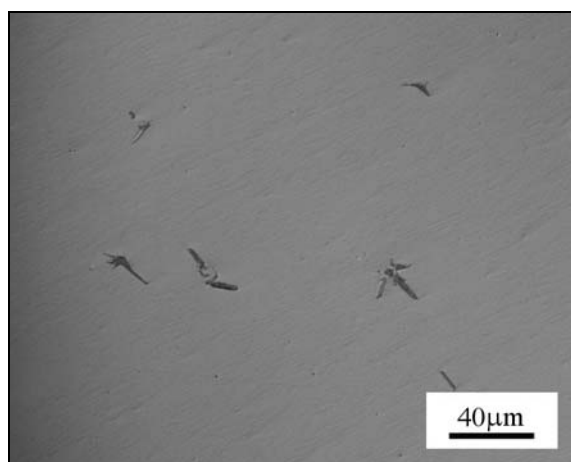


Fig. 5. Graphite in alloy E (annealed 1100°C/8 h).

microhardness are 443 HV 0.05 for matrix and 575 HV 0.01 for the rod-like particles. For the given content of carbon and according to the rolling temperature graphite should be present in the matrix as supposed by the phase diagram shown in Fig. 1.

The observed bright phase corresponds to graphite neither morphologically nor by the value of HV. This relates to κ -phase. Using XRD κ -carbide was identified (see pronounced (111), (200) and (220) reflections of κ -phase in Fig. 4). The structure did not change after annealing at 600 and 800°C.

The annealing at 1100°C/8 h (oil quench) changes the structure. κ -phase is dissolved and particles of dark phase (graphite) with size of 10–40 μm are appearing within the grains and along the grain boundaries – see Fig. 5. The dissolution of κ -phase is in agreement with the situation in the phase diagram.

3.3. Structure of alloy FA1.7C (F)

It is possible to observe both the pieces of darker phase (little greater) and pieces of brighter phase (size

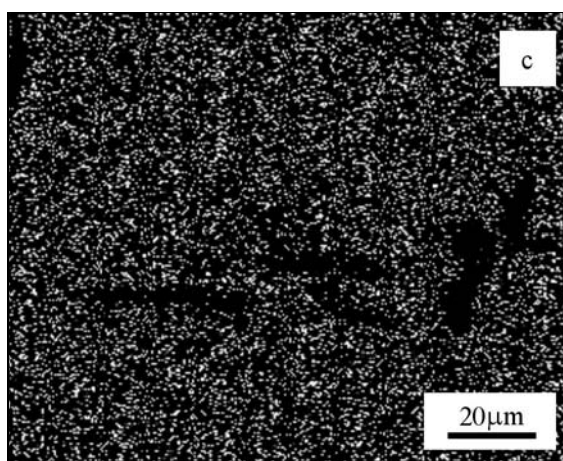
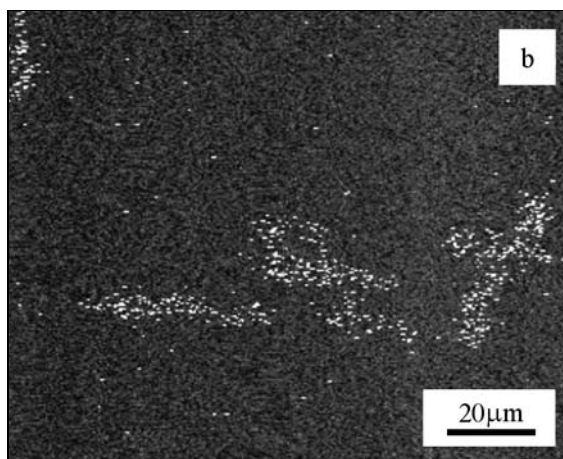
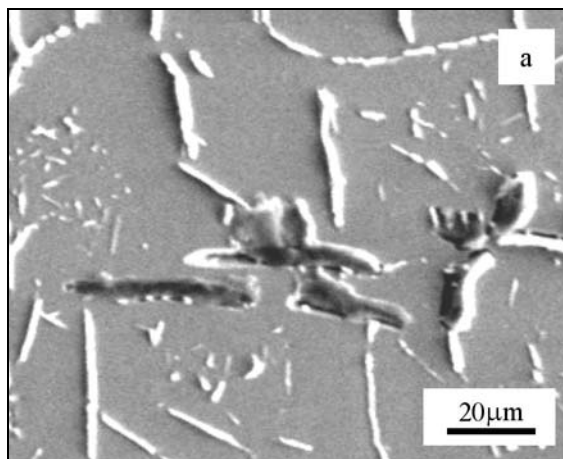


Fig. 6. (a) alloy F, original state, REM image, (b) alloy F, the same as in (a), image in $K_{\alpha}C$, (c) alloy F, the same as in (a), image in $K_{\alpha}Fe$.

20–50 μm) in the matrix (i.e. on the grey background), see Fig. 6a. The values of hardness are: matrix 357 HV 0.05, darker phase 140 HV 0.05, brighter phase 421 HV 0.01.

Using XRD the darker phase was identified to be graphite and brighter κ -phase. Also electron mi-

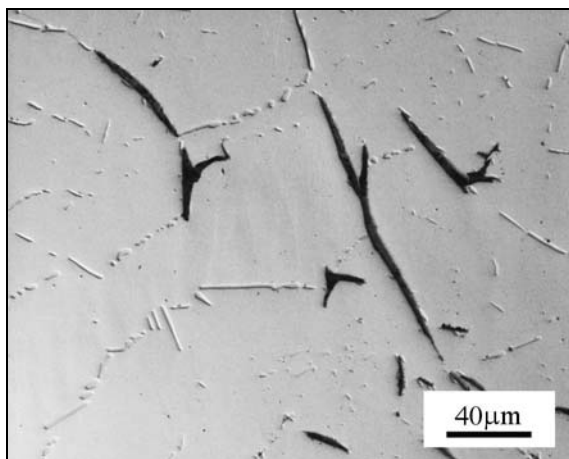


Fig. 7. Phases in alloy F are graphite (big dark phase) and κ -carbide (tiny bright phase), annealed 800°C/8 h.

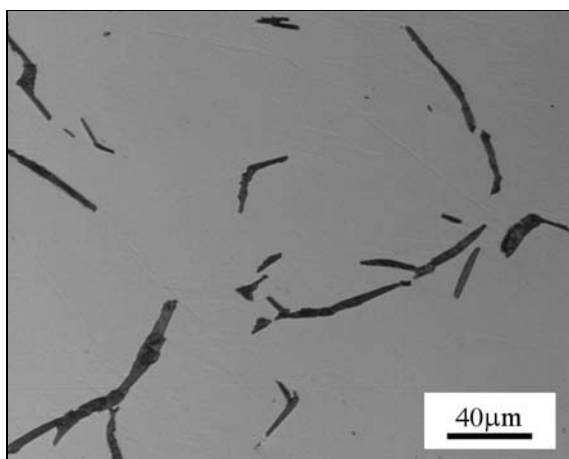


Fig. 8. Graphite in alloy F (annealed 1100°C/8 h).

croanalysis was used to confirm graphite particles. Using $K_{\alpha}C$ line and $K_{\alpha}Fe$ (Figs. 6b,c), the increased content of C or zero content of Fe are obvious. It was not possible to identify carbon in bright particles (κ -phase) according to low sensitivity of the equipment. The phase composition at 600°C/100 h and at 800°C/8 h is characterized by the substantial contribution of κ -carbide existing together with graphite lamellae – Fig 7. The phases were identified by XRD. Microhardness values also support the presence of κ -carbides: matrix 413 HV 0.05, graphite 161 HV 0.05, κ -phase 503 HV 0.01.

On the other hand graphite (hardness 79 HV 0.01) is the only phase in matrix after annealing at 1100°C/8 h. Lamellae up to 100 μm long (Fig. 8) are observed. The dissolution of κ -carbide increases the hardness of matrix to 478 HV 0.05.

XRD reveals weak but recognizable lines of κ -

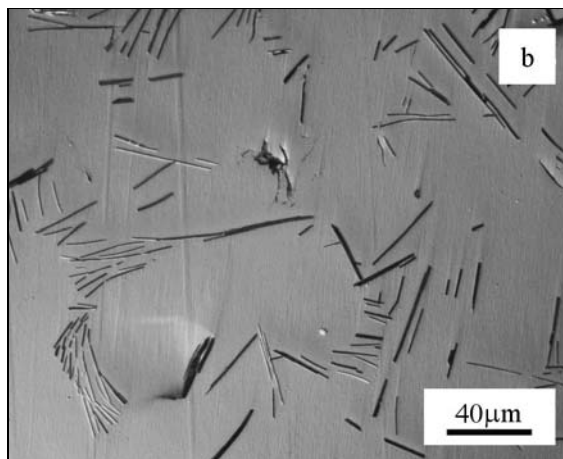
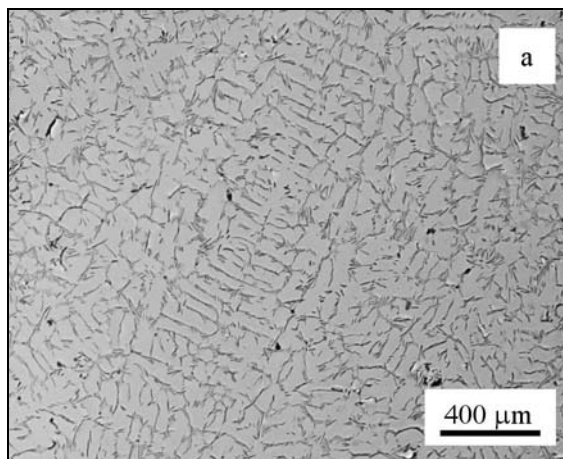


Fig. 9. (a) dendritic structure in alloy H, as cast, (b) dendritic structure in alloy H, detail.

-phase. The particles are probably very fine and cannot be identified by LOM.

3.4. Structure of alloy FA1.9C (H)

The composition of alloy FA1.9C is approaching to that of Pyroferal[®] (specially by the presence of Si). Dendrite structure is typical for the casting (hardness of the matrix 314 HV 0.1). Dendrites are formed by aluminium carbide Al_4C_3 (Fig. 9). The gradual dissolution of Al_4C_3 at 600°C is obvious. Figure 10 describes the situation after 1000 hours.

During annealing at 1000°C/8 h Al_4C_3 dissolves. Thus also the hardness of the matrix is enhanced: 495 HV 0.1. The phase composition was again verified by XRD.

3.5. Summary of experimental data

The knowledge about the presence of phases in the above studied alloys is summarized in Table 2. The summary obtains also the experimental methods used

Table 2. Table of observed phases and the art of identification

C (at.%)	Not annealed	Annealed at 600°C/100 h	Annealed at 800°C/8 h	Annealed at 1100°C/8 h
0.1 (D)	C as soluted in B2 LOM, HV	C as soluted in B2 LOM, TEM, HV	C as soluted in B2	C as soluted in B2 LOM, HV
0.8 (E)	κ LOM, HV	κ LOM, TEM, HV	κ LOM	G LOM, XRD, HV
1.7 (F)	$\kappa + G$ LOM, HV	$\kappa + G$ LOM, XRD, TEM	$\kappa + G$ LOM, HV	G + κ LOM, XRD, HV
1.9 (H)	Al ₄ C ₃ + G LOM, XRD	Al ₄ C ₃ + G LOM		Al ₄ C ₃ + G LOM, XRD, HV

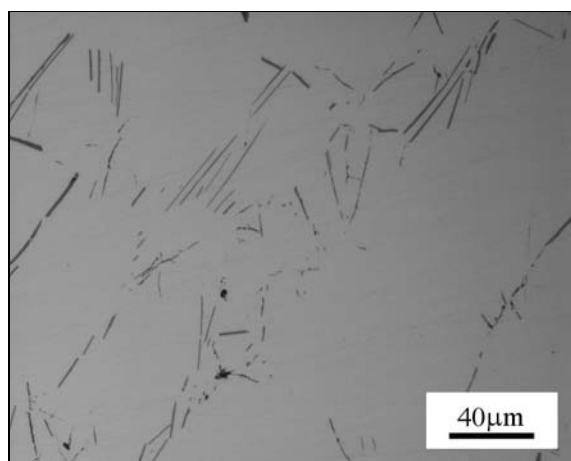


Fig. 10. Structure as in Fig. 9b after annealing at 600°C.

in individual cases. The small deviations compared to quasibinary diagram in Fig. 1 are obvious in Fig. 11.

4. Discussion

There is discrepancy concerning the region of existence of κ -phase. Its complete dissolution [4] should take place approx. at 950°C. In our experiment κ -phase is present both in the original state and after annealing at 1100°C/8 h.

The fields of existence of κ -phase are uncertain even after intensive work in the past [5–9]. Mostly these studies have failed to determine the borders of the existence of κ -phase. The most reliable informations are due to Palm and Inden [7] at 800, 1000 and 1200°C. They pointed out the difficulties in determining the exact position of κ -phase, which arise from the precipitation of graphite, that yields metastable phase equilibria in expected κ -single phase field.

The results obtained here can be situated also into

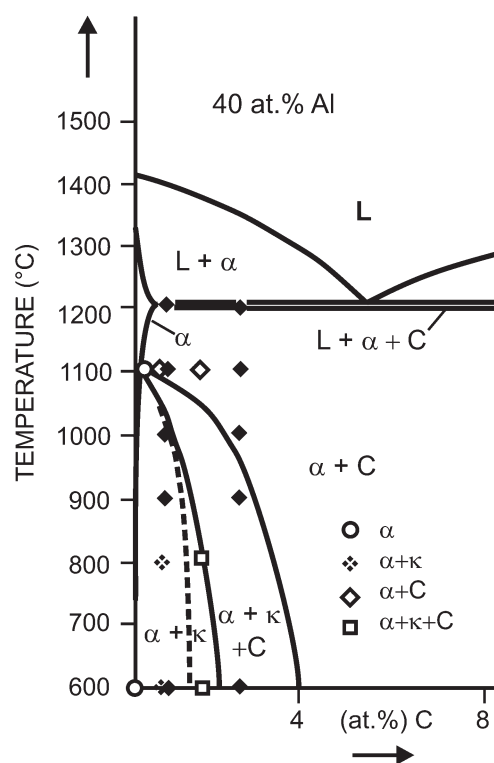


Fig. 11. Phase diagram Fe-40at.%Al-C as in Fig. 1 completed by data obtained in this paper.

isothermal cuts through Fe-Al-C data [6] at 800°C and 1100°C.

800°C: Our data for alloys FA0.8C (E) and FA1.7C (F) do not fit into corresponding regions according to [6] – see Fig. 12. In both cases κ -phase was identified in a two-phase region $\alpha + C$. This disagreement can be improved moving three phase $\alpha + \kappa + C$ boundary into the position marked by dashed line in Fig. 12.

1100°C: The alloys E and F, i.e. FA0.8C and FA1.7C should be found in two-phase region $\alpha + C$. This was the case only for alloy E. In the alloy F κ -

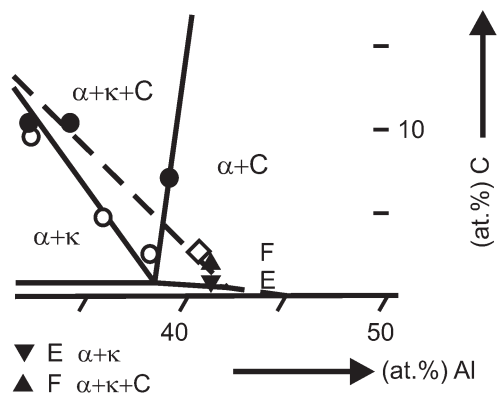


Fig. 12. Part of a ternary Fe-Al-C diagram at 800°C according to [6]. The results with alloys E and F are included.

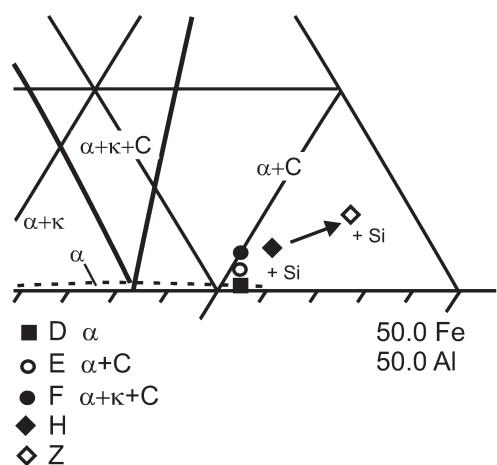


Fig. 13. Part of a ternary Fe-Al-C diagram at 1100°C according to [6]. The results with alloys E, F and H are included together with the alloys to be studied in the future.

-phase was present in little extent. Figure 13 should illustrate this situation. Also future procedure is illustrated: from alloy H the two alloys will be approached having the composition nearly identical to Pyroferal (Z), the first one without Si, the other one the same one but with Si.

Very interesting is the appearing of aluminium carbide Al_4C_3 in alloy FA1.9C, which is probably caused by the presence of Si. The increase of the concentration of Al is a matter of further experiments. Al_4C_3 fully dissolves at temperatures higher than 1100°C. Aluminium carbide is the phase observed in the binary system Al-C.

Very recently Ohtani et al. [10] calculated the ternary Fe-Al-C phase diagrams at 800, 1000 and 1200°C introducing CALPHAD method combined

with FLAPW (Full Potential Linearized Augmented Plane Wave) method. The results fit partly the investigation by Palm and Inden [7]. The very important point in the “story of κ -phase” is the chemical composition of κ -phase, which was reported [6] between $Fe_{3.2}Al_{0.8}C_{0.71}$ and $Fe_{2.8}Al_{1.2}C_{0.42}$.

5. Conclusions

The attempt was made to determine the phase composition of the Fe-Al- x C (at.%) alloys and to determine regions of existence for $Fe_3AlC_{0.5}$ (κ -carbide) and graphite phase as function of C content.

The methods used for such procedure were LOM, XRD, HV, and TEM combined with SAD.

As a result, small corrections both in the quasibinary Fe40Al- x C (at.%) diagram and in ternary Fe-Al-C phase diagrams are proposed.

Acknowledgements

The authors would like to dedicate this paper to Prof. RNDr. Zuzanka Trojanová, DrSc., on the occasion of her 65th birthday.

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