THE EFFECT OF Al AND C CONTENTS VARIATIONS ON THE PHASE COMPOSITION AND PHASE MORPHOLOGY OF PYROFERAL© TYPE IRON ALUMINIDES

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Abstract

Complex study of alloys based on FeAl aluminide was leading in the fifties of the last century to the proposal of. The composition of the binary Fe-Al alloy was modified by C and Si. This alloy with excellent corrosion and heat resistant properties was used to replace the high chromium and nickel alloyed cast iron.

The investigations performed recently on Fe-40 at.%Al type alloys with carbon contents 1.9-3.8 at.% and aluminium up to 43 at.% were designed to explain in more detail the origin of the structure and mechanical properties of the mentioned material.

It is the purpose of this contribution describes the effect of Al and C on the structure of iron aluminides with the composition of Pyroferal©. The appearing and morphology of carbide Al_4C_3 and of graphite is described in the as cast and annealed state.

Keywords: Intermetallic Alloys, Iron Aluminides, Pyroferal

1. INTRODUCTION

A possible method for improvement of creep resistant FeAl-type aluminides is the strenghening by second phase particles. One possibility is the addition of carbon. The strengthening is due to the formation of carbide particles, for example Fe3AlCn perovskite-type carbide or Al4C3 carbide.

On the same basis the alloy Pyroferal (44.6-46.5 at.% Al and 3.4-4.0 at.% C) was prepared in Czech republic as replacement of expensive nickel and chromium steels in the fifties of last century, analogous to Thermagal© in France or Tchugal© in Soviet Union. There are available very important results, which were achieved during the research between 1950 and 1962, based on the numerous research reports of Prof. J. Pluhař, Ing. M. Vyklický and Ing. H. Tůma, the scientists, who initiated and completed the research leading to the development of Pyroferal© (members of the VÚMT Prague - the predecessor of the present SVÚM Běchovice a.s.).

Pyroferal© offered quite impressive results in high temperature corrosion resistance. It was tested against air atmosphere, vanadium pentoxide, molten glass, carburization, nitration and the atmosphere of the natural gas cracking generators. Good results were also described in wear resistance and hardness due to appearance of hard and brittle aluminium carbide Al4C3 [1,2].

The recent attention was given to FeAl based alloys with composition similar to Pyroferal. The effect of carbon addition on the phase composition and morphology [3,4] and the effect on the high-temperature deformation properties [5] were discussed.

The present paper completes structural studies of alloys with composition within range of Al and C close and identical as Pyroferal.The main task was to find the effect of deviations of Al and C content compared to Pyroferal.

2. MATERIALS AND EXPERIMENTAL METHODS

The research was performed with alloys of the composition given in Table 1 (at.% are used). Compositions are also given in ternary diagram in Fig. 1a,b.

Table 1 The chemical composition of the alloys

Alloy	at. %				
	Fe	Al	C	Si	Denoted
FA 3.7C Si	balance	45.1	3.7	0.8	P
FA 3.8C Si	balance	43.3	3.8	0.8	N
FA 4.0C Si	balance	44.7	4.0	0.8	R
FA 4.9C Si	balance	43.0	4.9	0.7	O

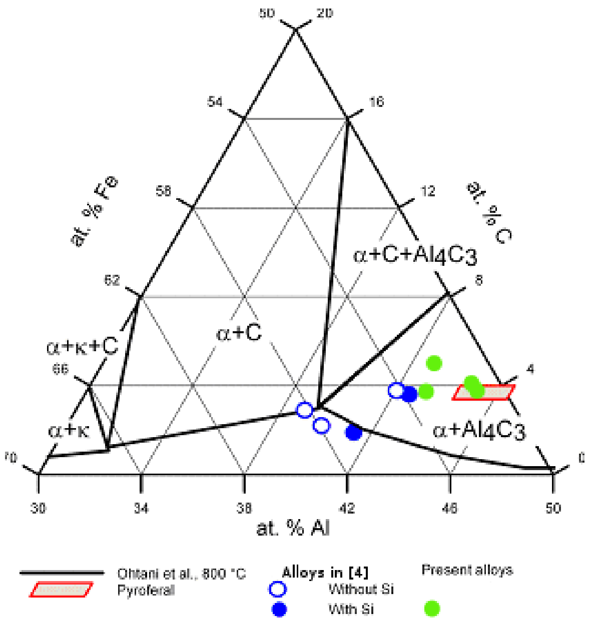

Fig. 1a. Ternary Fe-Al-C phase diagram [6] for 800°C with concentrations within this paper and corresponding to [4]

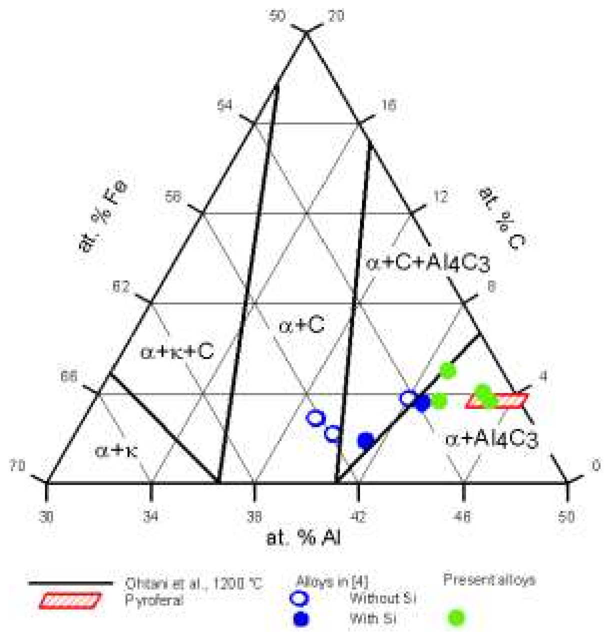

Fig. 1b. Isotermal section of ternary phase diagram via Ohtani for 1200°C with composition points

All alloys were prepared by vacuum melting in the induction furnace. The cast slabs (cross section 19,5x 40 mm, length 200 mm) were rolled at 1230°C in the five steps on the laboratory rolling mill K350.
The chemical composition of all alloys were determined using spectral analysis by optical emission spectrometer LECO GDS 750a.
The morphology of phases was studied by light optical microscopy (LOM) with Nomarski-contrast application and scanning electron microscopy (SEM). The phases were determined by energy dispersive X-ray spectroscopy and X-ray diffraction analysis (XRD).
The heat treatment with different temperature, time and cooling was used :

- annealing at 800°C 8h, quenching into the mineral oil
- annealing at 1100°C 24h, quenching into the mineral oil
- long-time annealing at 1150°C 200h, cooling in air

3. RESULTS AND DISCUSSION

The composition of alloys P and R is very similar with respect to carbon and aluminium contents, the content of silicon is almost identical. To see the effect of Al content on the morphology and structure of phases these two alloys can be compared with alloy N containing less Al. To observe the effect of C content on phase structure, the alloy N is compared with alloy O.

3.1 The effect of Al content on the phase structure (the comparing of alloys P and R to N)

The increasing Al content has no effect on the phase composition of alloys in as cast state – it is identical in all alloys. Three phases (Fig. 2, XRD in Fig. 3) are present – eutectic mixture of the solid solution α (bright area in Fig. 2) and fine needle-like Al_4C_3 phase, and clumps of coarse graphite lamellae (size 50-200μm) - see detail in Fig. 2.

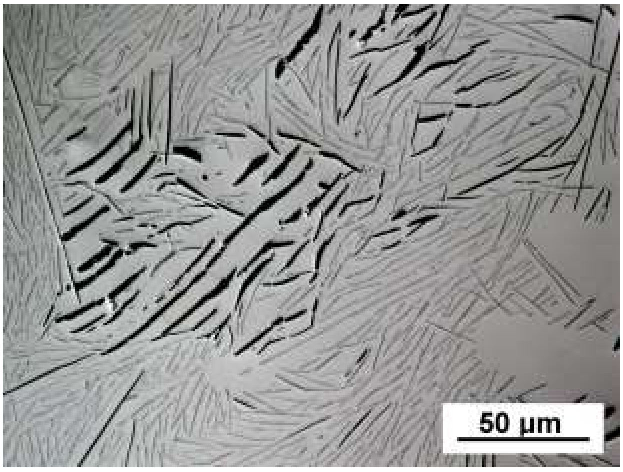

Fig. 2. Alloy P, as cast state (bright matrix, fine lamellae of Al4C3 carbide and black graphite lamellae), LOM

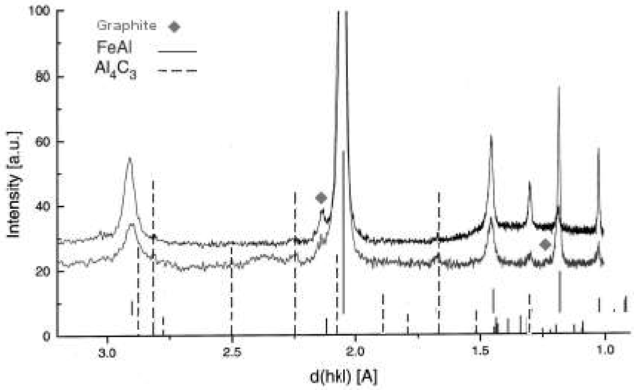

Fig. 3. The diffraction curve of as cast (lower curve) and annealed state (upper) of alloy N

The differences appear in the structure after high-temperature heat treatment (annealing at 1100°C and 1150°C): graphite lamellae are totally dissolved in alloys R and P, whereas graphite flakes remain in the structure of alloy N - compare Fig. 4 and 5. EDX and XRD analyse were used for verification of graphite and carbide phase. A small volume fraction of needle-like carbide phase is conserved in the structures of all alloys after annealing 1100°C /24h/ oil, long time annealing leads to gradual solution needle-like carbide phase – see Fig. 4, 5. It is obvious that bigger carbide needles are getting coarsen during annealling, Fig. 5.

Higher amount of coarse carbide lamellae are present in the structures of alloys R and P (higher Al content) than in the structure of alloy N (lower Al content) - compare Fig. 4 and 5.

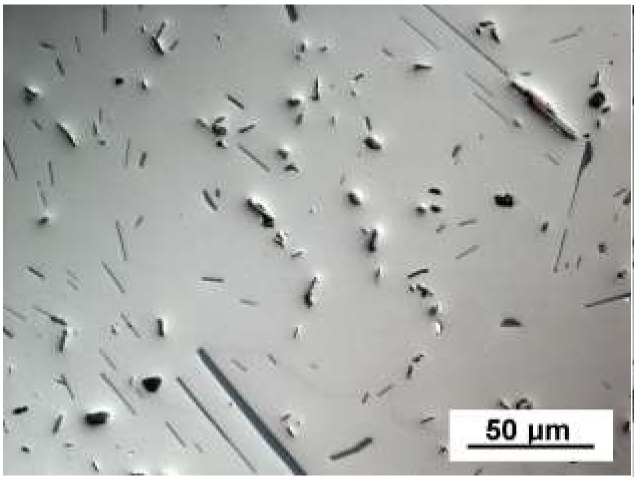

Fig. 4. Alloy N, after annealing 1150°C /200h/ air, Al_4C_3 lamellae, graphite in flakes , LOM

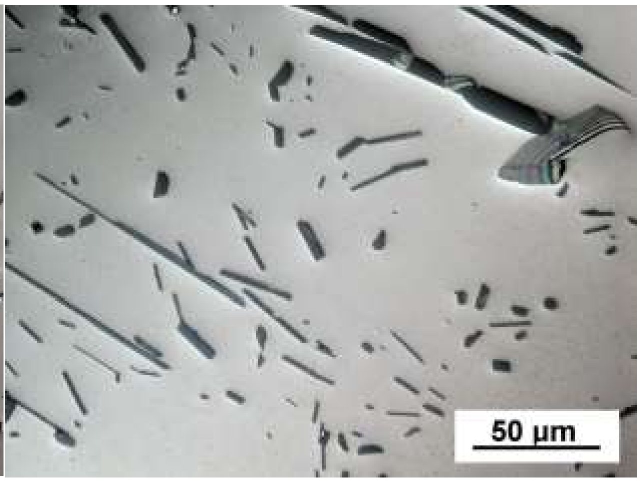

Fig. 5. Alloy R, after annealing 1150°C /200h/ air, Al_4C_3 lamellae, LOM

Higher Al content (more than 44 at.%) for Pyroferal type alloys may be recommended on the basis of the comparison of structure: the higher Al content leads to conservation of carbide Al_4C_3 after annealing, whereas lower Al content leads to conservation of the graphite phase. The structure with higher quantity fine needle-like Al_4C_3 phase is advantageous for high - temperature properties of iron aluminides [5] as well as absence of the soft graphite phase.

3.2 The effect of C content on the phase structure (the comparing of alloys N and O)

The alloy N and O have comparable Al content, but marked difference of carbon content – alloy O has higher C content than alloy N. Phase composition of alloy O is the same as of N alloy: solid solution FeAl, Al_4C_3 carbide and graphite (verified by XRD) - but morphology of phases is very different.The carbide Al_4C_3 occurs only as fine needle-like phase in the as cast structure of alloy N with lower C, whereas coarse carbide plates and fine needle-like carbide are present in the structure of alloy O with high C (and Fig. 7). Graphite is present as lamellae and flakes in both alloys.

Differences are much more pronounced after heat treatment: the fine needle-like Al_4C_3 dissolves gradually, but flakes of graphite remain in alloy N (lower C). In the structure of alloy O (high C) fine needle-like phase dissolves gradually too, but coarse carbide plates are coarsening even more (compare Fig. 7 and 8). Small amount of graphite flakes remain in the structure of alloy O too.

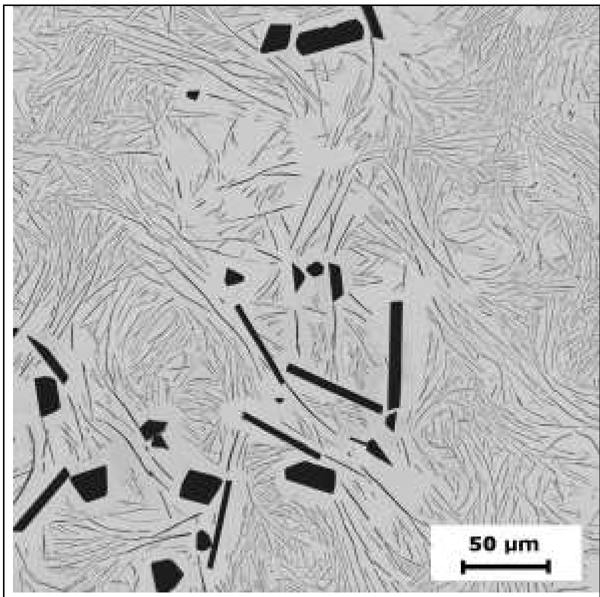

Fig 7. Alloy O, as received, Al_4C_3 as plates and fine needle-like phase, BSE image

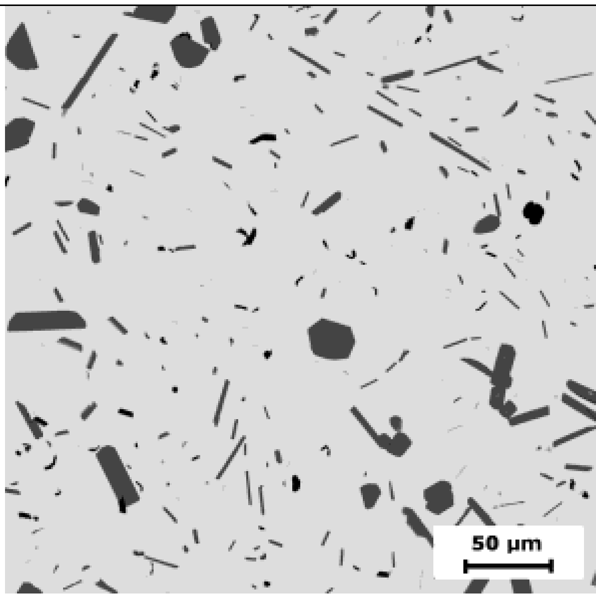

Fig. 8. Alloy O, after annealing1150°C/200h, Al_4C_3 as plates and coarse needle, graphite, BSE image

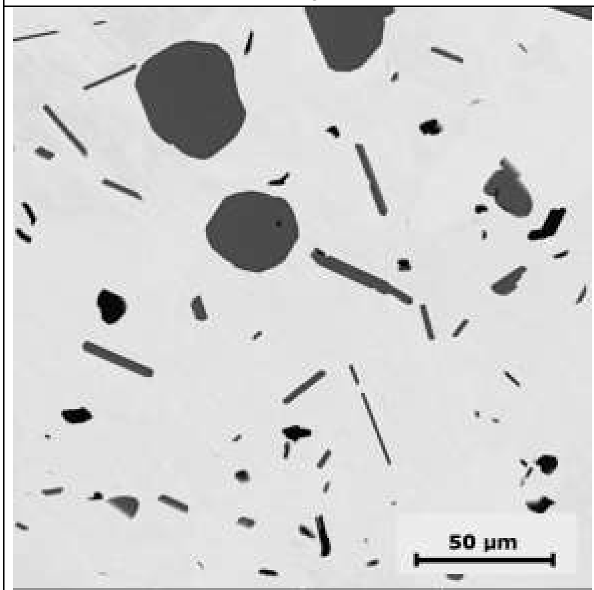

Fig.9a. Alloy O, after annealing 1150°C/200h, BSE image – small black particles are graphite, dark grey Al_4C_3

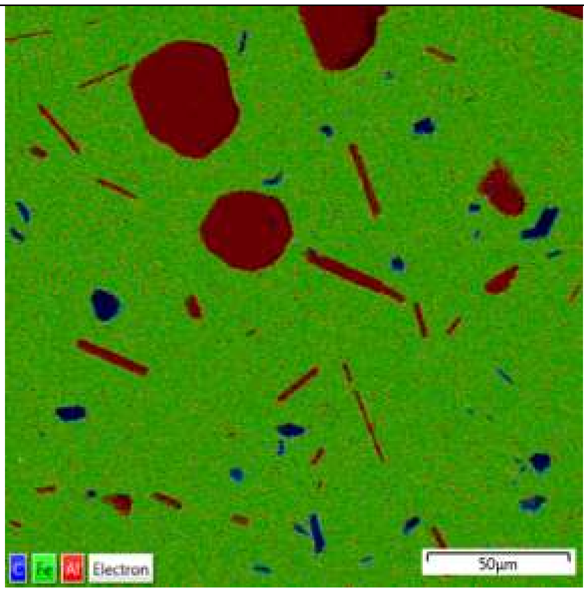

Fig 9b. Alloy O, after annealing 1150°C/200h, EDX map image – phase verification: small blue particles are graphite flakes, red particles are Al_4C_3

The high C content leads to the formation of carbide plates in as cast state and to further coarsening during heat treatment. These brittle carbide plates introduce into the matrix internal stresses and decrease brittle fracture resistivity. Their high hardness increases wear resistence of alloys.

3.3 The phases in the investigated alloys

The main problem of phase composition is presence Al_4C_3 carbide. It is given in older version of Fe-Al-C diagram by Vogel and Mader [7] – they indicated this carbide at concentration about 44 at.% Al and 1at.% C. It is in agreement with older experiments of Vyklický and Tůma [1]. This phase is not mentioned for such concentrations later by Nishida [8] and recently by Palm and Inden [9]. The addition of silicon is supposed to support the formation of Al_4C_3 carbide [4].

The summary of the phase composition of the alloys after heat treatment is given in Table 2. The presence of phases is compared to ternary diagram of Ohtani et al. [6] (800°C and 1200°C), see Fig. 1a and 1b.

Table 2 – The summary of the phase composition of the alloys after heat treatment.
(C) …minority phase, C_F….graphite in flakes form, C_L….graphite in lamellae form

Alloy	Ohtani 800°C	Present paper 800°C	Ohtani 1200°C	Present paper 1150°C
N	**FeAl + Al_4C_3**	**FeAl+Al_4C_3+(C_F)**	**FeAl + Al_4C_3**	**FeAl+Al_4C_3+(C_F)**
P	**FeAl + Al_4C_3**	**FeAl+Al_4C_3+(C_L)**	**FeAl + Al_4C_3**	**FeAl + Al_4C_3**
R	**FeAl + Al_4C_3**	**FeAl+Al_4C_3+(C_L)**	**FeAl + Al_4C_3**	**FeAl + Al_4C_3**
O	**FeAl + Al_4C_3**	**FeAl+Al_4C_3+(C_F)**	**FeAl+Al_4C_3+(C)**	**FeAl+Al_4C_3+(C_F)**

It is obvious, that graphite is present in the structure an extra phase if compared to Ohtani diagrams. Its presence in the structure is reported Palm and Inden [9].

The annealing at 800°C / 8h induced refinement of structure for all alloys, i.e. the solution of coarse graphite lamellae compared to as cast. The residual graphite in the structure of all alloy as lamellae (alloys P and R) or flakes (alloys N and O) was observed – see Tab 2.

The long-time annealing at 1150°C /200h induces redistribution of Al_4C_3 needles (alloy N). Very pronounced coarsening of Al_4C_3 plates is observed in alloy O. Little graphite flakes were conserved in both alloys with lower Al content (N, O) .The graphite was totally dissolved in alloys with higher Al content (P,R). The coarsening of needle-like phase Al_4C_3 was noticed in these alloys (Fig. 5)

CONCLUSIONS

- **reduction of Al content below 44 at.%** leads to the presence of the soft graphite phase in the structure after high-temperature (both 800 and 1150°C) heat treatment
- **increase of C content over 4 at.%** leads to the formation of very coarse and brittle phase- Al_4C_3 plates, which is disadvantageous for deformation properties
- annealing at 800°C contributes to dissolution or to refinement of coarse graphite phase in alloys P,R and N
- the presence of Al_4C_3 carbide corresponds to the ternary diagram of Ohtani [6]
- the presence of the residual graphite is in agreement with the ternary diagram of Palm and Inden [9]

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