The effect of heat treatment on the structure and high – temperature strength of Fe₃Al – based iron aluminide doped by carbon and carbide-forming element

Martin Švec, Věra Vodičková, Pavel Hanus, Vojtěch Keller

Technical University of Liberec, Studentská 1402, Liberec, Czech Republic

Material Science Department

E-mail: martin.svec@tul.cz

Abstract. A structural study as well as the determination of σ₀.₂ compression yield stress at high temperatures have been performed on the Fe₃Al-based iron aluminide doped by Nb (5 at. %) and C (1.5 at. %). The carbon occurrence leads to the formation of three-phase structure. Fe₃Al matrix, niobium carbides and (Fe, Al)₂Nb Laves phase were observed in the structure of investigated alloys. Precipitates were inhomogeneously distributed in as cast state alloy. The annealing at 1000 °C for 50 hrs. leads to more homogenously distribution of secondary phase particles and also to refinement of grain size. The strengthening mechanism of material at high temperatures was detected as a combination of strengthening by incoherent precipitates (NbC and Laves phase) and a solid solution hardening by Nb atoms. Effect of two reinforcing mechanisms together with homogeneously precipitate’s distribution increase the values of σ₀.₂ compression yield stress about 50 MPa in whole measured temperature range (600 – 800 °C) in comparison to similar intermetallic’s system Fe-Al-Zr-C.

Phase composition of the alloy was studied by means of scanning electron microscopy (SEM) equipped by energy dispersive X-ray spectrometer (EDX). The electron backscattered diffraction (EBSD) was used for phase verification and grain size visualization.

1. Introduction

Alloyed iron aluminides have been recognized as candidate materials for high-temperature (it means temperature range 600 – 800 °C in case of Fe-Al-X alloy) structural application due to their very good corrosion resistance as well as their low density. The binary iron aluminides show reasonable strength and ductility at room temperature but only mediocre creep resistance at high temperatures [1-4].

The creep resistance improvement is possible by the secondary phase particles, which should form the stable and fine dispersion. These particles may be precipitates of carbides, borides or intermetallic phases [5, 6]. In last period the research works are focused on the improvement of high-temperature creep resistance by alloying of binary alloys by carbide-forming or boride-forming elements [7, 8]. Many recent studies have examined a variety of carbide or intermetallic precipitates such as Laves phase [9]. An alternative method of material reinforcement is incorporation of the secondary phase through directional solidification of eutectic alloys [10].

Recently the iron aluminides doped by carbon and other carbide – forming element(s) are investigated [11, 12]. The primary motivation is to use inexpensive raw materials as we are currently focusing on high performance materials but made from cheaper raw materials (and cheap raw iron usually used to be contaminated by carbon). In the present the focus is on the materials with the high utility materials properties but made from cheaper raw materials. At the same time, it is required the
restriction of use of strategic element such as Cr, Ni etc. The research of iron aluminides doped by carbon and carbide-forming elements is also motivated by options to replace expensive high alloyed (especially alloyed by high amount of strategic Cr) steels P-91 or P-92 type by these intermetallic alloys in high – temperature applications. Fe-Al-Nb system is one of the Fe-Al-X systems which are of interest for development of Fe-Al – based alloys. Niobium has potential for both solid solution hardening and precipitation strengthening. The precipitation of intermetallic Laves phase (Fe, Al)2Nb in Fe-Al-Nb system can lead to improvement of high-temperature creep resistance of alloys. The knowledge of Laves phase (Fe, Al)2Nb formation processes and their stability against coarsening during high-temperature annealing is very important. It was shown that fine precipitates of Laves phase were able to produce good strengthening for temperatures up to ca. 750 °C [13]. Recently the effect of heat treatment on the composition of niobium doped iron aluminides was investigated [14, 15]. The aim of article is to show the effect of heat treatment on the structure of alloy and to compare the influence of different type of carbide forming elements on high-temperature strength.

2. Materials and experimental methods
The investigated alloys were prepared by vacuum induction melting and casting. The nominal chemical composition of the samples is given in table 1. Two states of alloy were investigated for selection of sample with suitable microstructure for the next high-temperature compressive testing. Initial state was as cast (marked as FA5Nb1C AC), annealed state (marked as FA5Nb1C HT) was heat treated at 1000 °C for 50 hrs. and air cooled. The microstructure was observed in five different cross-section places of cast in both alloys. No structure differences were observed between each places. The samples for study of microstructure were oxide-polished by suspension OP-S in the final step. This leads to the enhance of visibility of carbide phase in topographical contrast [16]. The structure was investigated by scanning electron microscopy (SEM) Tescan Vega 3SBH equipped with Oxford X-Max20 detector for energy dispersive analysis (EDX) and by SEM Zeiss Ultra Plus equipped with Oxford X-Max20 EDX detector and Nordlys Nano EBSD detector used for phase verification and for determination of grain maps (scanning area was 500 x 700 μm in both cases, step was 2 μm). The samples (prisms 6 x 6 x 10 mm) for high – temperature compression tests were prepared from annealed material (FA5Nb1C HT) by spark machining. The compression yield stress σ0.2 was measured using INSTRON 1186 at temperature 600, 700 and 800 °C with the initial strain rate 1.2 x 10^-4 s^-1. The values of yield stress were measured twice for each temperature. The obtained results were comparable.

The values of high-temperature strength of alloy FA5Nb1C was compared with values for 1181 alloy [17] for comparison of carbide – forming element effect. The quantitative chemical composition of 1181 alloy (Fe-26Al-4.9Zr-1.4C in at. %) was analogous to FA5Nb1C, structure was different only in type of carbide-forming element (Zr by 1181, Nb by FA5Nb1C). The samples for compression test had the same dimensions (prisms 6 x 6 x 10 mm) and surface finishes (polished). They were also made from annealed material (at 1000 °C for 50 hrs.), the applied initial strain rate was the same. The carbon occurrence in Fe-Al-Zr system shifts the phase stability and therefore no τ phase was observed in the case of 1181 alloy. (Fe, Al)2Zr Laves phase and ZrC were present in the structure only.

Table 1. The nominal chemical composition of investigated samples.

| sample    | chemical composition (at. %) |
|-----------|------------------------------|
| FA5Nb1C   | bal. 26.1 4.9 1.4            |

2
3. Results and discussion

3.1. Structure of FA5Nb1C AC

The structure of matrix was coarse-grained with average grains dimensions of micrometers of 75 ± 30 μm – see figure 1 (the dark areas enclosed by light grey net of precipitates) and figure 2 (EBSD grain size measurement). Two types of precipitates were observed in the structure. The niobium carbides (NbC) were situated inside of grains. Distribution of these precipitates was very inhomogeneous (figure 1) and their size was about 5 μm. Second type of particles was determined as Laves phase (Fe, Al)_2Nb. Laves phase started to nucleate along the grain boundaries and some particles were present also inside the grains (see detail in figure 1). Laves phase particles had elongated shape with dimensions about 1 μm or less. Small amount of added niobium was also dissolved in the matrix (see table 2). Preliminary phase identification was performed by EDX and verified by EBSD (see table 2 and figure 3).

No eutectic net formed in the structure of FA5Nb1C AC sample in comparison to the alloy with the same content of aluminum and niobium but without addition of carbon (Fe – 27.3 Al – 4.8 Nb alloy) [14]. In FA5Nb1C AC there appeared the precipitates NbC in the structure preferably due to high affinity of carbon to niobium. The niobium excess is sufficient for Laves phase (Fe, Al)_2Nb formation, but it is not sufficient for formation of Fe3Al matrix + (Fe, Al)2Nb eutectic net as in the case of Fe – 27.3 Al – 4.8 Nb alloy [14].

Table 2. The average chemical composition of phases in FA5Nb1C AC alloy.

| phase              | Fe       | Al       | Nb       | C  |
|--------------------|----------|----------|----------|----|
| Matrix (at. %)     | balance  | 26.6 ± 0.2 | 1.0 ± 0.1 | -  |
| Laves phase (at. %)| balance  | 18.6 ± 0.8 | 27.3 ± 0.5 | -  |
| NbC (at. %)        |          |          |          | verified by EBSD as NbC |

Figure 1. The structure of alloy FA5Nb1C AC (SE detector). Dark grey – Fe3Al matrix, Light grey – (Fe, Al)_2Nb Laves phase (in detail: arrow 1 – Laves phase on grain boundaries, arrow 2 – Laves phase inside the grain.), White – NbC.
3.2. Structure of FA5Nb1C HT

No changes were observed in the phase composition after heat-treatment. Annealing at 1000 °C for 50 hrs. had beneficial effect on the NbC distribution in the structure of investigated sample. Niobium carbides are presented inside the grains and their distribution is much more homogeneously (figure 4). It is clearly visible from figure 4 (in comparison to figure 1) that NbC were not only redistributed, but also they were partly refined (size in order of units of micrometers). On the other hand, precipitates of Laves phase got coarsen and individual small particles on grain boundaries (and partly also inside the grains) started to coagulate. Annealing at 1000 °C for 50 hrs. also significantly refined the grains of matrix. The average grains size was 19 ± 6 μm after heat treatment (see EBSD figure 5).

3.3. The yield stress at high-temperatures

The structure of FA5Nb1C HT sample was more homogenous, therefore this material was chosen for all high-temperature compressive tests. As expected the values of yield strength $\sigma_{0.2}$ of FA5Nb1C were decreasing with the increasing temperature. However, they were sufficient for high-temperature applications up to 700 – 800 °C.

The values of high-temperature yield stress of investigated FA5Nb1C HT sample were compared with values for the alloy 1181 [17] – see figure 6. The carbides and the precipitates of Laves phase
formed in both alloys. The $\sigma_{0.2}$ values of FA5Nb1C were about 30 – 50 MPa higher at all temperatures than that for 1181 [17]. There may be more reasons for the higher strength of FA5Nb1C at high temperatures:

The first, in FA5Nb1C there is a combination of strengthening mechanism by incoherent precipitates (NbC and Laves phase) and strengthening by solid solution hardening (Nb). Solid solubility of niobium is about 1 at. % in Fe$_3$Al matrix [18], however the solid solubility of Zr is only 0.1 at. % [19, 20] and therefore the effect of incoherent precipitates in 1181 takes place in strengthening only. The second reason is the secondary phases form and distribution. No coarsening of precipitates during compression tests was noticed (see figure 7). The Laves phase precipitates and NbC are very homogeneously distributed in the structure of FA5Nb1C. The grain boundaries are also reinforced by fine precipitates of Laves phase. These precipitates could work as obstacles for dislocation movement and they also act similar effect as hardening phase in composites. No cracks appeared in the matrix or in precipitates after high-temperature compressive tests (see Fig. 7 – structure after deformation at 800 °C). Compared to that, the eutectic net of Fe$_3$Al matrix + (Fe, Al)$_2$Zr Laves phase and inhomogeneously distributed clusters of ZrC were observed in the structure of 1181 [17]. These clusters of brittle ZrC could act as initial areas for cracks. Also, the Laves phase in 1188 is present only as part of eutectic net. There are the places completely without precipitates in the structure. No dislocation movement obstacles were present in these places between eutectic net.

It can be summarized, that both Nb and Zr have high affinity to carbon. However, the carbon affinity to Zr is slightly higher than that to Nb and it is the reason, why the clusters of ZrC are formed in 1181 [17] and why they are stable also after annealing [21]. The clusters of NbC formed to a certain extent also in FA5Nb1C AC, but they dispersed after annealing.

**Figure 6.** The dependence of $\sigma_{0.2}$ yield stress on the temperature for investigated FA5Nb1C and 1181 [17].

**Figure 7.** The structure of FA5Nb1C HT alloy after compression deformation at 800 °C (BSE detector).

4. Conclusions

The structures of investigated samples are three-phase – Fe$_3$Al matrix + NbC niobium carbides + (Fe, Al)$_2$Nb Laves phase (phase composition was the same for both as cast and heat-treated states).

The heat-treatment at 1000 °C for 50 hrs. leads to achieve of the homogeneous structure and technically usable values of high-temperature strength.

The strengthening mechanism in FA5Nb1C is a combination of strengthening by incoherent precipitates (NbC and Laves phase) and a solid solution hardening by Nb atoms. However, the precipitate’s strengthening holds the main effect.

The addition of Nb + C into Fe$_3$Al iron aluminides increases the high – temperature strength more effectively than alloying by Zr + C (the values of yield stress of FA5Nb1C are about 30 – 50 MPa higher at all tested temperatures than those for 1181 alloy [17]. This could be caused by more
homogeneous distribution of precipitates in case of FA5Nb1C HT alloy as well as by additional effect of solid solution hardening by Nb atoms.

Acknowledgements
This publication was written at the Technical University of Liberec as part of the project "The study and evaluation of the structure and properties of metallic and non-metallic materials" with the support of the Specific University Research Grant, as provided by the Ministry of Education, Youth and Sports of the Czech Republic in the year 2019 and as part of the project supported by the Ministry of Education, Youth and Sports of the Czech Republic and the European Union - European Structural and Investment Funds in the frames of Operational Programme Research, Development and Education - project Hybrid Materials for Hierarchical Structures (HyHi, Reg. No. CZ.02.1.01/0.0/0.0/16_019/0000843).

References
[1] Morris D G and Munoz - Morris M A 1999 The influence of microstructure on the ductility of iron aluminides Intermetallics 7 p 1121
[2] Mc Kamey C G 1994 Physical Metalurgy and processing of Intermetallic Compounds p 351
[3] Stoloff N S 1998 Iron aluminides: present status and future prospects Mater. Sci. Eng. A 258 p 1
[4] Deevi S C and Sikkia V K 1996 Nickel and iron aluminides: an overview on properties, processing and applications Intermetallics 4 p 357
[5] Palm M, Schneider A, Stein F and Sauthoff G 2005 Strengthening of iron aluminide alloys for high-temperature applications Mater. Res. Soc. Symp. Proc. 842 p S1.7.1
[6] Palm M 2005 Concepts derived from phase diagram studies for the strengthening of Fe – Al based alloys Intermetallics 13 p 1286
[7] Mc Kamey C G and Maziasz PJ 1998 Heat treatment effects for improvement creep-rapture resistance of a Fe3Al-based alloy Intermetallics 6 p 303
[8] Dobeš F, Kratochvíl P, Pešička J and Vodičková V 2015 Microstructure and creep behavior of Fe-27Al-1Nb alloys with added carbon Metall. Mater. Trans. 46A p 1580
[9] Stein F, Palm M and Sauthoff G 2005 Mechanical properties and oxidation behaviour of two-phase iron aluminium alloys with Zr(Fe, Al)2 Laves phase or Zr(Fe, Al)12 τ1 phase Intermetallics 13 p 1275
[10] Milenkovic S and Palm M 2008 Microstructure and mechanical properties of directionally solidified Fe-Al-Nb eutectic Intermetallics 16 p 1212
[11] Schneider A, Falat L, Sauthoff G and Frommeyer G 2003 Constitution and microstructures of Fe-Al-M-C (M=Ti, V, Nb, Ta) alloys with carbides and Laves phase Intermetallics 11 p 443
[12] Falat L, Schneider A, Sauthoff G and Frommeyer G 2005 Mechanical properties of Fe-Al-M-C (M=Ti, V, Nb, Ta) alloys with strengthening carbides and Laves phase Intermetallics 13 p 1256
[13] Moriss D G, Munoz – Morris M A and Baudin C 2004 The high-temperature strength of some Fe3Al alloys Acta mater. 52 p 2827
[14] Švec M and Vodičková V 2014 The effect of niobium addition and heat treatment on the phase structure of Fe3Al – type intermetallic alloys Manufacturing Technology 14 p 456
[15] Morris D G, Munoz – Morris M A, Requejo L M and Baudin C 2006 Strengthening at high temperatures by precipitates in Fe – Al – Nb alloys Intermetallics 14 p 1204
[16] Kejzlar P, Švec M and Macajová E 2014 The usage of backscattered electrons in scanning electron microscopy Manufacturing Technology 14 p 333
[17] Kratochvíl P, Vodičková V, Král R and Švec M 2016 The effect of Laves phase (Fe, Al)2Zr on the high-temperature strength of carbon-alloyed Fe3Al aluminide Metall. Mater. Trans. 47A p 1128
[18] Prymak O and Stein F 2010 Solidification and high-temperature phase equilibria in the Fe-Al-rich part of the Fe-Al-Nb system Intermetallics 18 p 1322
[19] Raghavan V 2010 J. Phase Equi. Diff. 31 p 459
[20] Kratochvil P, Kejzlar P, Král R and Vodičková V 2012 The effect of Zr addition on the structure and high temperature strength of Fe-30 at. % Al type alloys Intermetallics 20 p 39

[21] Palm M 2014 Max – Planck Institut für Eisenforschung GmbH, Düsseldorf, unpublished research