

High temperature properties of non-critical Fe-Al alloys doped by non critical or “slightly–critical” elements

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Abstract. Iron aluminides were developed as an alternative to stainless steels after World War II. The main intended impact was to save strategic elements (chromium or nickel). The result of these investigations was development of registered alloys as Pyroferal (Czechoslovak Republic), Thugal (Soviet Union) or Thermagal (France). The investigation of these type alloys continued in the nineties thanks to technological progress. In this time iron aluminides seems to be promising material with very good corrosive and environment resistivity. The mechanical properties of binary iron aluminides (Fe-Al) are average at higher temperatures but strengthening effect of alloying elements is significant. The aim of the article is to show influence of non-critical additives (such as C, Ti, Zr) and also “slightly critical” elements as e.g. Ce, Nb on high temperature creep properties of alloys.

1. Introduction

Iron materials alloyed by aluminium as heat resistant materials were known even before 1900 [1]. In the thirties of the 19th century the investigations were focused on the effect of Al adding to cast iron [2, 3].

The long-term interest for aluminium modified iron materials started in Europe scale after World War II. The initial focus on the effect of adding Al to white and grey cast iron was replaced by the idea to substitute chromium and nickel in heat resistant cast iron in later studies. These efforts resulted in large-scale production of ternary Fe-Al-C materials. The result of these investigations was development of new materials such as Tchugal in former Soviet Union, Thermagal in France or Pyroferal in former Czechoslovakia.

Pyroferal alloy was the result of very detailed research of such type of materials initiated in Czechoslovakia in the 1950s of the last century. The quasi-binary phase diagrams [4,5] for Fe-xAl-yC were constructed based on the investigation of the phases in the Fe-Al-C system. Pyroferal alloy [6] exhibited good mechanical properties at higher temperatures and especially very good corrosion resistance (the layer of aluminium oxide that was formed protected the material comparatively better as the substituted materials highly alloyed by Ni and Cr). Also resistance against aggressive environment (against the atmosphere of the natural gas cracking generator or against molten glass) or carburization was tested with very successful results.



Recently the „like Pyroferal“ materials were tested again to find out the reasons for the excellent H.T. corrosion resistance and mechanical properties [7, 8]. Namely the dependence of the creep properties and structure at 600°C on the content of carbon and silicon was tested [9].

On a global scale the intensive research focused on aluminides was started in the late nineties. The alloys with FeAl and Fe₃Al matrix were also investigated in Czech Republic, especially at the Charles University in Prague, in cooperation with research teams in Liberec, Brno and Ostrava.

2. Improvement of high-temperature mechanical properties of Fe₃Al-type Iron Aluminides

In general, iron aluminides exhibit excellent corrosion and environment resistance, they have low density and – important attribute for industrial use – they are affordable. Fe₃Al-type iron aluminides with D0₃ lattice have good strength at moderate temperatures due to high degree of crystallographic order.

Current research is focused on improving high-temperature (H.T.) tensile and creep properties of Fe₃Al-type iron aluminides. The task to enhance the H.T. mechanical properties of Fe₃Al based alloys can be arranged by using of different methods [10]:

- strengthening by solid solution hardening which is useful for addition of small amount of ternary elements such as Cr, V, Mo and Ti,
- strengthening by incoherent precipitates which may be either formed due to ternary additions of Zr, Ta, Nb or Ti in higher concentrations (diverse phases originate according to high-temperature isothermal section of phase diagrams) or carbide and boride precipitates, which need additions of C or B (also as quaternary to the above mentioned elements),
- strengthening by coherent precipitates as one of the most effective methods (B2 in A2 and vice versa for Fe-Al-Ni-Cr alloys or B2+L2₁ in Fe-Al-Ta system),
- strengthening by increased crystallographic order which stabilizes the D0₃ structure to higher temperatures (e.g. Fe-Al-Ti).

Another alternative to increase H.T. mechanical properties is represented by directionally solidified eutectic alloys, Fe-Al-Nb for example, that showed a higher creep resistance only at 650°C – 750°C compared with the as-cast alloys of about the same composition. The creep resistance at higher temperature remained at the same level [11].

An especially effective method is based on the addition of elements with a low solubility in the Fe Al-matrix. From this point of view, the alloying by zirconium may be used. The beneficial effect of zirconium addition on creep resistance was first written by McKamey and Maziasz [12, 13]. The incoherent phases are typically formed in iron aluminides without carbon addition, i.e. pure ternary Fe–Al–Zr alloy. Even small amounts of Zr leads to the precipitation of Laves-phase (Fe,Al)₂ Zr or τ₁-phase (Fe,Al)₁₂ Zr particles that may limit of dislocation motion during deformation.

Zirconium was tested as an additive to Fe₃Al-type iron aluminide to enhance the H.T. tensile by Kratochvíl et al. [14,15] The formation of ZrC particles, which contributed to improvement of tensile creep properties, was described. Kratochvíl et al. [16] compared influence of Zr combined with TiB₂ on creep resistance of Fe₃Al-type alloy with chromium content. Significant influence of Cr (strengthening by solid solution hardening) was described by McKamey in [17]

In Fig. 1, the comparison of Minimum Creep Rates (MCR) at 600°C is shown for alloys doped by Zr combined with TiB₂ (pink areas) investigated in [16], doped by Zr (FA6, FA11) [14], by TiB₂ (FA3) and by Ce (FA1) [18]. It was demonstrated, that the combination of additives Zr + TiB₂ in the tested alloy does not improve the creep resistance. The material slightly alloyed with Zr with fine dispersion of ZrC particles is obviously the best of the compared iron aluminides [16]. Therefore, Zr was confirmed as suitable element for enhancement of H.T. mechanical properties of Fe₃Al-based iron aluminides.

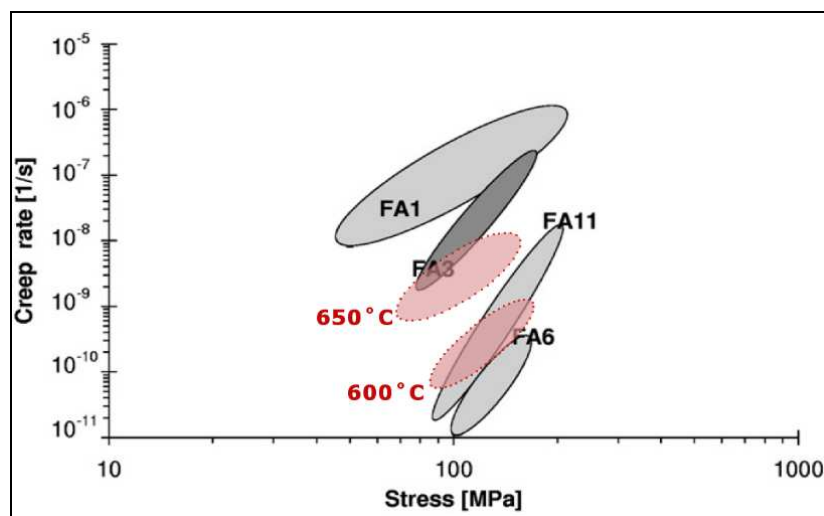


Figure 1. The comparison of MCR at 600°C [16]

If the low cost of the raw materials is required, the presence of carbon in raw Fe is unavoidable. Carbon can be also used as one of the cheapest available alloying elements, with its low solubility in iron and a negligible solubility in aluminium. Moreover, carbon content appears to be beneficial in suppressing the hydrogen embrittlement at grain boundaries. The research focused on carbon addition [19, 20] confirmed that the influence of carbides morphology and distribution on the properties of alloys with 24 - 28 at. % Al can be significant. Baligidad et al. [19] attributed the improvement in the mechanical properties at elevated temperature to the presence of the Fe_3AlC phase (carbide κ) as well as the interstitial carbon in the matrix. On the other hand, according to Schneider et al. [20], the carbide κ does not enhance of the H.T. strength efficiently due to fast coarsening.

While the influence of zirconium or carbon on alloy strengthening has been described in great detail, less attention has been devoted to the combined additions of zirconium and carbon. This summarizing article purpose is to present a part of research focused on the common effect of zirconium and carbon with the aim to find an optimal concentration ratio of the additive elements to increase H.T. mechanical properties.

3. The effect of combined addition of zirconium and carbon on creep resistance of Fe_3Al -based alloys - results and discussion

The effect of phase composition on H.T. mechanical properties of Fe_3Al -based iron aluminides **with chromium addition** (3.7 at. %) was investigated through H.T. properties testing and demonstrated via microstructure analysis [21]. The alloys were prepared by vacuum induction melting and casting, the casts were rolled at 1200°C.

Phase composition of low-alloying iron aluminides (Zr content 0.2-0.3 at. %, C content 0.2-0.6 at. %) was investigated by means of scanning electron microscopy and energy dispersive X-ray analysis and subsequently verified through electron diffraction by TEM. Creep tests with stepwise loading in temperature range 600 – 800°C were used. Tests were carried out in a protective atmosphere of dry purified argon. Creep resistance was compared through Minimum Creep Rate values [21]. This paper studied the effect of the $c(\text{Zr})/c(\text{C})$ ratio on the microstructure and H.T. mechanical properties of Fe_3Al -type aluminides. Two cases are distinguished: materials with Zr excess and those with C excess. Based on comparison of phase composition of alloys alloyed with Zr and C simultaneously, the relative ratio of zirconium-carbon concentrations can play a significant role. With respect to the ratio $c(\text{Zr})/c(\text{C})$, there may be two cases of phase formation:

- with the carbon predominance, the zirconium affinity toward the carbon prefers the formation of carbides ZrC , and it is the majority phase.

- with the Zr predominance, ZrC is again preferred (due to the high affinity of Zr to C), but after consumption of carbon, there will be enough Zr to form of the Laves phase.

An exact knowledge of nature of the secondary phase particles can contribute to the improvement of creep resistance at high temperatures. This research confirmed that the concentration ratio of two additives (zirconium and carbon) influenced the phase structure of the investigated undeformed alloys in agreement with the relationships in the Fe–Al–Zr ternary phase diagram. The secondary phase particles - Laves phase λ_1 (Fe,Al)₂ Zr and ZrC - were distributed primarily along grain boundaries, with some distribution in the grains as well – Fig. 2. Their strengthening role is limited to blocking the grain boundaries' motion because the effect of these particles inside the grains (owing to large distance between the particles) is insignificant. During the H.T. deformation two different metastable phases (Fe_{1-x}Al_x)₃Zr and Fe₂Zr originate and interact with dislocations. The changing density and size of these particles with temperature explains the described change in the creep behavior [21].

The combined effect of carbon and zirconium on creep resistance can be evaluated from the point of view of the concentration ratio $c(\text{Zr})/c(\text{C})$. The stress for producing a creep rate of 10^{-7} s^{-1} is presented as a function of this ratio - Fig. 3. An increase of this stress with $c(\text{Zr})/c(\text{C}) > 1$ is in agreement with contribution of the Laves phase to creep resistance [21].

In follow-up research [22, 23, 24] on the influence of ratio was carried for **Cr-free** iron aluminides. The examined alloys were prepared by vacuum melting and casting; Zr was added in metallic form.

Due to higher amount of zirconium in the investigated alloys, Laves phase was present as eutectic mixture with matrix. It has been demonstrated that the relative ratio of carbon-zirconium concentrations affects the amount of Zr remaining for Laves phase formation, which subsequently affects volume fraction of Laves phase. Finally, resulting H.T. mechanical properties are influenced by volume fraction of the eutectic mixture of Laves phase and matrix. The influence of the volume fraction of the eutectic (Laves phase and matrix mixture) on the strengthening was confirmed through H.T. yield stress in compression for materials with minimum amount of carbon (Fig. 4) [22] as well as materials with higher carbon (Fig. 5) [23].

The effect of zirconium/carbon ratio on creep resistance of chromium-free iron aluminides was also investigated [24]. The alloys with higher amount of zirconium and different carbon contents (0.06 to 3.46 at. %) were tested. The examined alloys were prepared by vacuum melting and casting. The samples were subjected to stepwise loading, where the load was changed after the steady-state creep

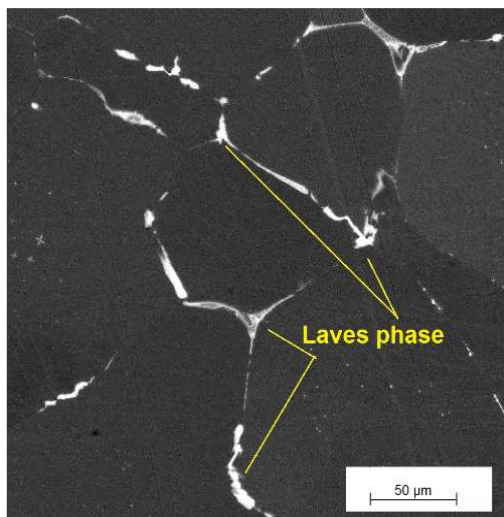


Figure 2. The structure of 1A alloy [21]

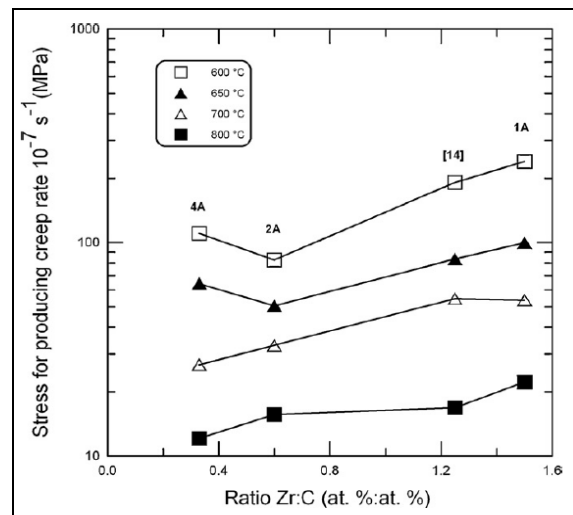


Figure 3. The stress necessary to produce a creep rate of 10^{-7} s^{-1} as a function of $c(\text{Zr})/c(\text{C})$ [21]

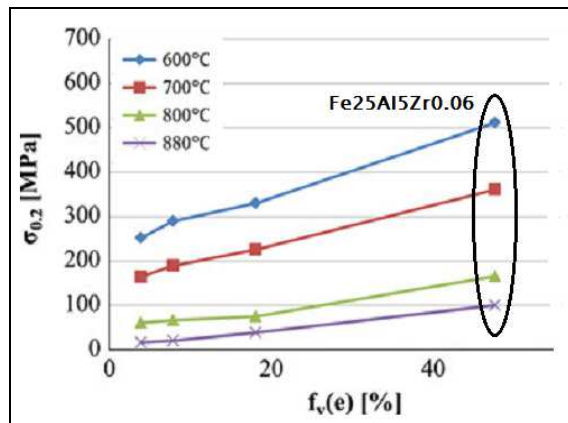


Figure 4. Dependence of $\sigma_{0.2}$ of the as-cast Fe-25Al alloys on the volume fraction of the eutectic $f_v(e)$ at various temperatures [22]

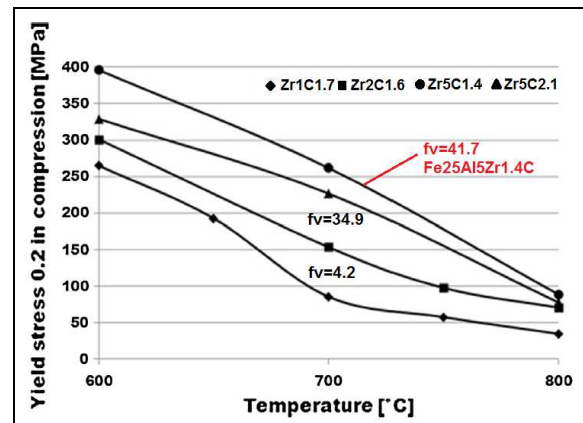


Figure 5. The dependence of the yield stress $\sigma_{0.2}$ on temperatures for as-cast alloys [23].

rate was established for a given load. Creep resistance was evaluated using dependence of the creep rate on the applied stress σ at the various temperatures. Stress exponent n and activation energy of creep were compared. Results were also discussed in terms of the concentration ratio of $c(\text{Zr})/c(\text{C})$. In Fig. 6, the stress for producing a creep rate of 10^{-7} s^{-1} is presented as a function of this ratio again. It is obvious that an increase of the creep resistance with increasing ratio Zr/C is in agreement with the behavior observed previously in alloys with lower concentrations of Zr and with Cr addition [21].

The effect of concentration ratio corresponds with the relationships in the Fe–Al–Zr ternary phase diagram (and its potential extension by adding carbon). It was confirmed that the presence of C reduces the amount of Zr that is available for the formation of the Laves phase and/or other Zr-phases that is why the creep resistance at 973 K (700 °C) is reduced [24].

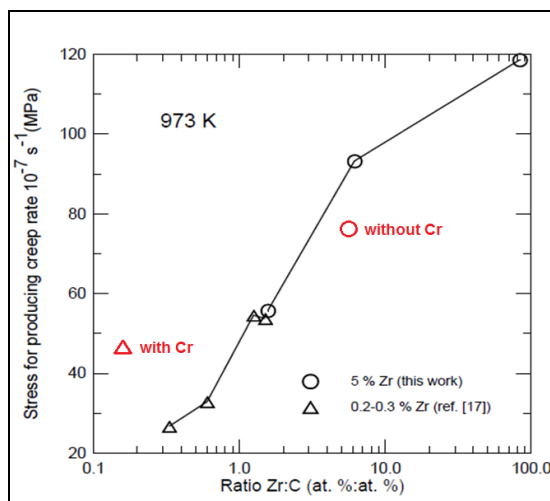


Figure 6. The stress necessary to produce a creep rate of 10^{-7} s^{-1} as a function of $c(\text{Zr})/c(\text{C})$, [17] in Fig = [21] in this paper

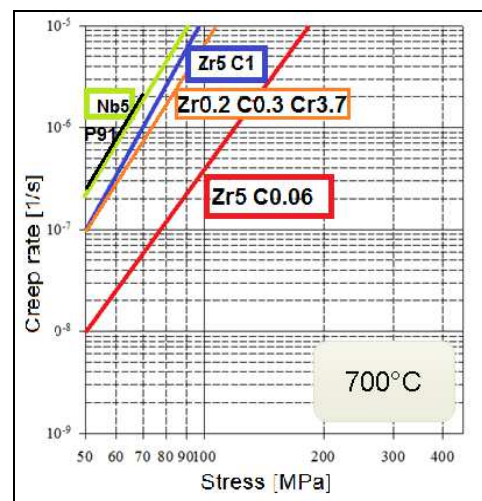


Figure 7. The comparison of creep rates at 700°C of alloys mentioned in this work

The comparison of creep rates of alloys mentioned in this work is given in Fig 7. Alloy Zr0.2C0.3Cr3.7 represents the material with Cr addition tested in [21]. Alloys Zr5C0.06 and Zr5C1 are chromium-free materials investigated in [24]. The creep rate of alloy with 5 at. % Nb [25] is

shown, because there is similarity between Fe-Al-Zr and Fe-Al-Nb systems especially with regard to region of Laves phase. In the Fe-Al-Nb system, the strengthening effect of the solid solution hardening must also be taken into account [26]. The values of P1 steel creep rate [27] are given as a representative of alloys with good creep properties. Based on this comparison it can be assumed that strengthening of Fe₃Al-type iron aluminides by chromium (critical element) - i.e. strengthening by solid solution hardening - can be fully replaced by the Laves phase strengthening due to alloying with zirconium (non-critical element), taking into account the "a priori" presence of carbon in the alloy.

4. Conclusion

With simultaneous alloying with zirconium and carbon, the ratio of their concentrations must be taken into account. As well as with zirconium alloying, if common quality iron is used for production of alloy.

The present of carbon always reduces the amount of zirconium available to produce the reinforcing Laves phase. By increasing the concentration ratio $c(\text{Zr})/c(\text{C})$, creep resistance increases.

This ratio also affects the amount of Zr that may contribute to the formation of a fine dispersion of the particles of other phases during creep deformation. These fine particles can act the function of obstacles to move the dislocations.

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