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High Alloy Steels

Iron Based Materials With Improved Oxidation Resistance Prepared By Powder Metallurgy

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Abstract
If oxidation resistance of iron based materials at elevated temperatures is required stainless steels like 316L are used. However the manufacturing process of stainless steel parts is more expensive compared to conventional Fe-based materials. The approach of the presented work is the development of oxidation resistant Fe-based materials using a cost effective technology. Aluminium and/or Silicon were used as alloying elements added to iron as a pre-alloyed powder (CuAl, NiSi). The sintering of the mixtures consolidated at 600MPa was performed at 1120°C under hydrogen. During sintering a liquid phase is formed at 1000°C leading to a homogeneous distribution of the alloying elements in the already formed iron skeleton. The investigation of mechanical properties have shown that strength and ductility values are comparable to copper alloyed iron based materials. The oxidation resistance is considerably improved and comparable with 316L up to temperatures of 800°C.

Introduction
Sintered parts made from PM iron based materials with high corrosion resistance nowadays are ferritic, chrome alloyed or austenitic chrome nickel sintered steel. Manufacturing of these products is connected with high costs. The powders from these alloys are expensive compared with other powders for the production of sintered steel parts. The compactibility of these powders is moderate and there are high demands on the sintering conditions. The sintering temperature for these materials has to be in the range of 1150 °C and 1250 °C or more [1]. Additionally a high partial pressure ratio between hydrogen and water vapour is necessary and carbon-containing components have to be prevented in the sintering atmosphere, because of the chromium carbide formation which results in a reduction of the chromium content available for the formation of a passivating layer. Instead of the cost effective endogas atmosphere cracked ammonia gas or pure hydrogen have to be used.
Beside chromium and nickel also silicon and aluminium are applicable as alloying elements for iron in order to improve corrosion resistance. For example cast iron with silicon contents from 4 to 6 % is used as a high temperature material in the heating-plant construction for annealing container, glass forms etc.. Aluminium-alloyed cast iron can also be used (2 % C, 5 % Si, app. 7 % Al). Highly alloyed cast iron with 2 to 3.5 % C, 5 % Si, partly also 3 to 7 % Cu and about 1 % Cr and a nickel content from 13 to 20 % is particularly stable against oxidizing inorganic acids and high temperature oxidation. The corrosion behaviour of these materials can be compared with cast steel alloyed with nickel and chromium [2].
There are several attempts to use aluminium as an alloying element in iron based materials prepared by powder metallurgy [3, 4]. The use of elemental iron and aluminium powders results in melting of aluminium at the melting point of 660°C. The melt penetrates the iron powder particle surfaces and intermetallic phases (aluminides) are formed which is connected with a swelling effect [5].

Without special powder treatments like high energy milling [5] aluminium alloyed sintered iron can not be prepared.
Another way would be the use of pre-alloyed powders prepared by atomization. These powders are generally hard and cannot be consolidated by die pressing to a sufficient density and green strength. Moreover aluminium oxide layers on the surface of the pre-alloyed powder particles result in problems during sintering of such powders.
Up to now the interest in PM Fe-Si-alloys was limited to the production of soft magnetic sintered part. [6] These materials require relatively high sintering temperature of 1250 °C [7].

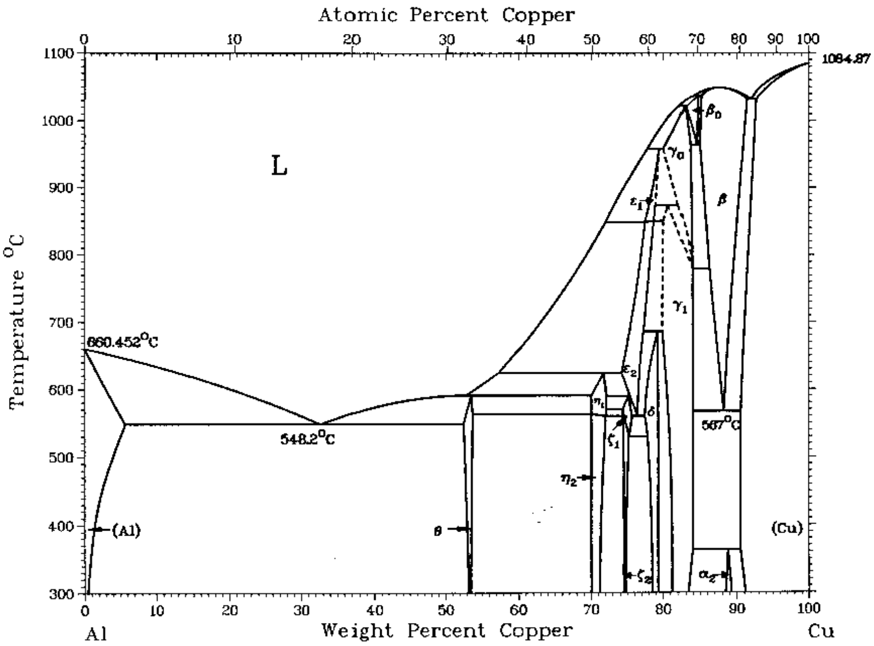

Fig. 1 Phase diagram Copper-Aluminium [8]

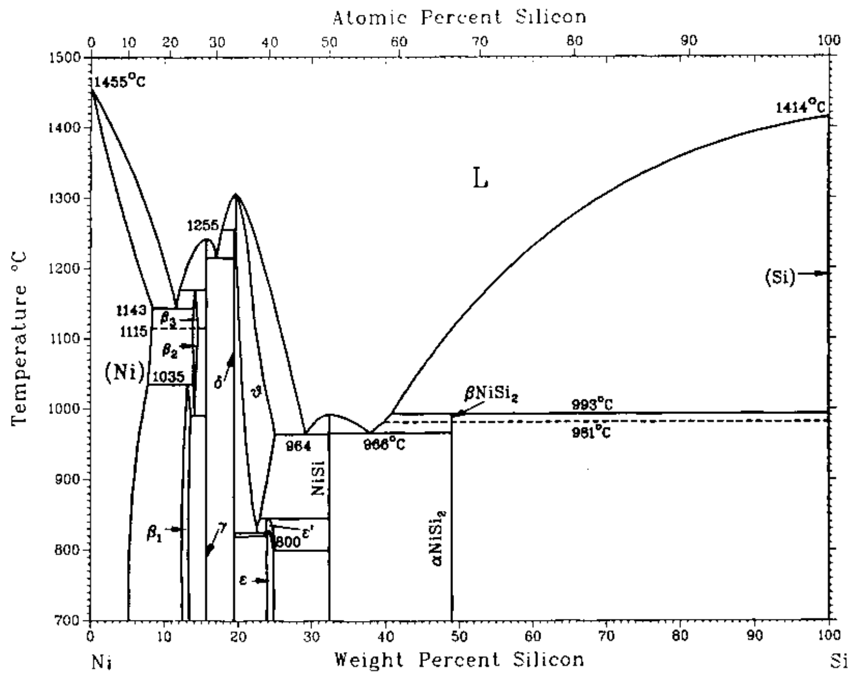

Fig. 2 Phase diagram Nickel-Silicon [8]

The presented idea is focused on the development of sintered steel parts with increased resistance against corrosion and/or high temperature oxidation which can be manufactured economically. The alloying elements aluminium or silicon are incorporated in the iron matrix by using a master alloy powder. The melting point or melting interval of such master alloy is only little below the sintering temperature of iron. The other components of the master alloy are the alloying elements of iron like copper of nickel. Due to the limited amount of the master alloy added to the iron powder, the compressibility is sufficient and the green parts can be sintered at 1120°C under endogas which is important from the economical point of view.
One example of such master alloy is an material consisting of 20 weight % aluminium and 80 weight % copper. Fig. 1 shows the phase diagram of the copper-aluminium system. It can be seen that an alloy with 20 weight % aluminium and 80 weight % copper has an melting interval from 960°C up to 1010 °C. Adding 30% of such master alloy to iron powder result in an alloy with the following composition: 70 % iron, 24 % copper and 6 % aluminium.
A further interesting system which was investigated is nickel-silicon (Fig 2). The composition 33% silicon and 67% nickel corresponds to the intermetallic phase NiSi, which melts at approximately 990 °C. Adding 18% of such a NiSi powder to iron result in an alloy with the composition: 82% iron, 12% nickel and 6% silicon.

Experiments

The master alloy powders 80Cu/20Al and 66Ni/33Si were prepared by melting with subsequent crushing of the ingots and finally milling. Due to the brittleness of such alloys crushing of ingots and milling in order to prepare a powder with a mean particle size of app. 10 µm was possible.
The powder was mixed with sponge iron powder NC 100.24. Every mixture contains 0,8wt.% Kenolube. Table 1 displays the four alloying compositions which were prepared.

Alloy	copper (wt.%)	aluminium(wt.%)	nickel (wt.%)	silicon (wt.%)	iron (wt.%)
FeCuAl12-3	12	3	-	-	85
FeCuAl24-6	24	6	-	-	70
FeNiSi12-6	-	-	12	6	82

Table 1 Composition of the alloys

The silicon content chosen in FeNiSi12-6 is comparable with the aluminium content of the aluminium alloyed iron based materials. Consequently a comparison of properties and oxidation resistance between Al-alloyed and Si-alloyed iron based materials should be possible.
From the manufactured mixtures samples for the mechanical test according to DIN/ISO 2740 were pressed with a pressure of 600 MPa. Sintering was performed under hydrogen at 1120 °C for all alloys mentioned in Table 1.
The oxidation behaviour was determined by thermal cycling under air up to temperatures of 820°C. The weight change was detected.

Results and Discussion

The microstructure of the Al-alloyed and Si-alloyed Fe-based materials are shown in Figure 3 and 4. The microstructure demonstrates in both cases rounded pores. This pore morphology is a typical advice for the presence of a liquid phase during sintering. In Figure 5, 6 and 7 the density of the materials and the mechanical properties (tensile strength and elongation) are shown in comparison to pure iron, FeCu24 alloy and stainless steel 316L.

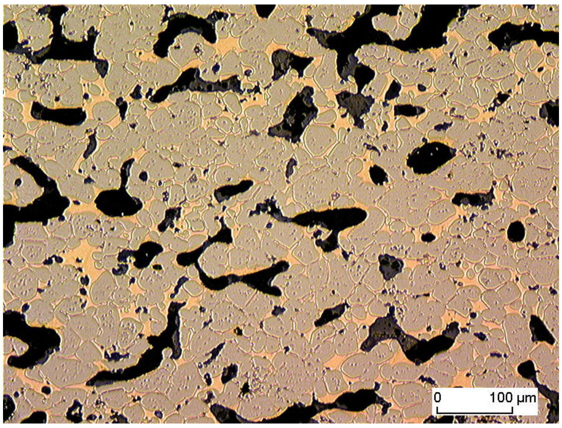

Fig. 3 Microstructure of Al-alloyed iron based material (FeCuAl24-6)

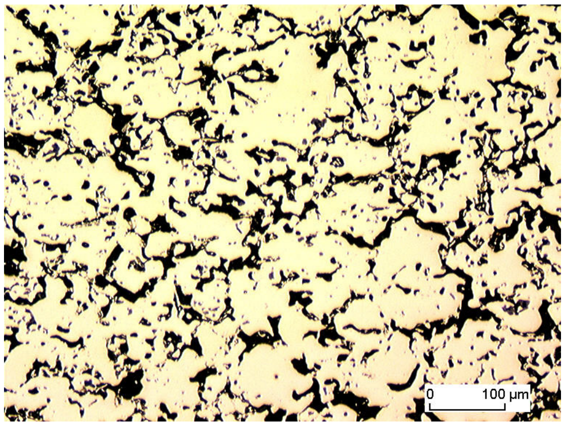

Fig. 4 Microstructure of Si-alloyed iron based material (FeNiSi12-6)

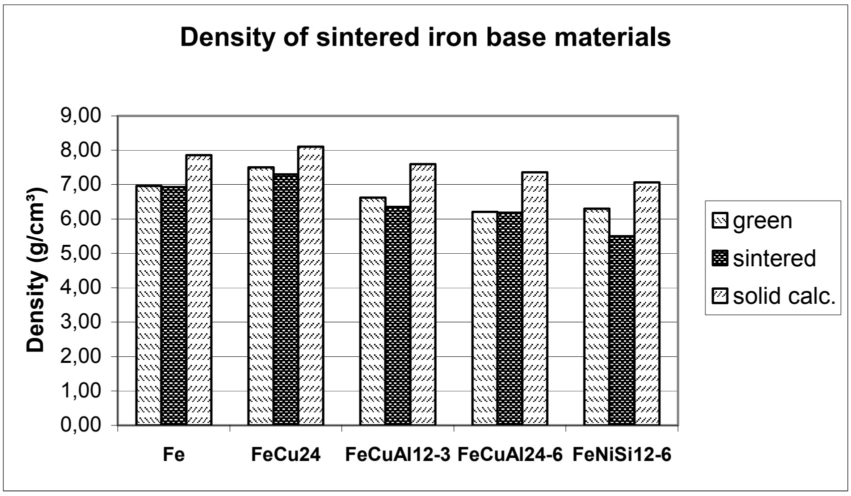

Fig. 5 Density of different iron based sintered materials (T_{sinter}=1120°C; 30min; H_2)

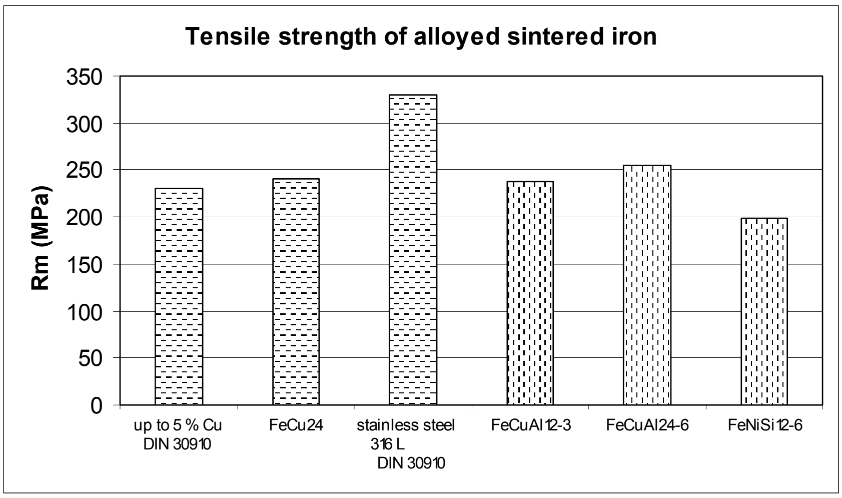

Fig. 6 Tensile strength of different iron based sintered materials (T_{sinter}=1120°C; 30min; H_2)

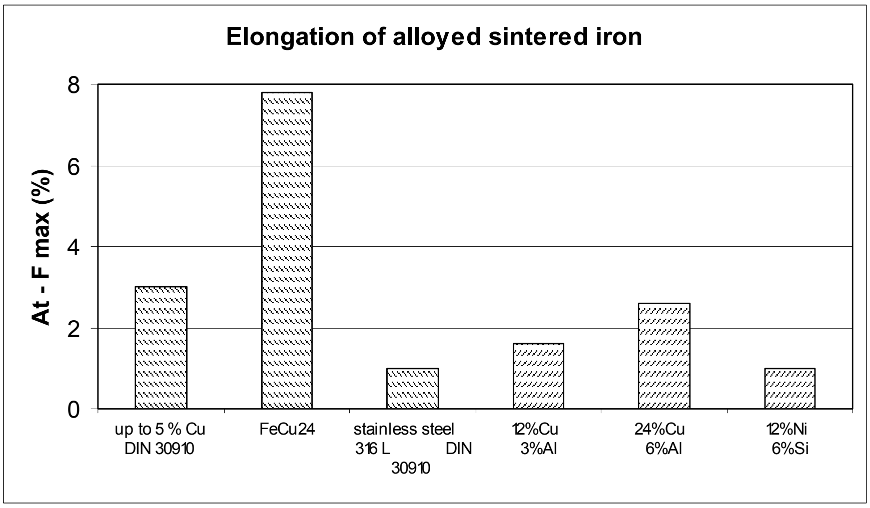

Fig. 7 Elongation of different iron based materials sintered materials (T_{sinter}=1120°C; 30min; H_2)

The addition of copper leads to a swelling of the samples which is also visible for the alloy with 3% Al. A higher Al-content (6%) leads to reduced swelling due to the higher amount of liquid phase. In the case of Si-alloyed iron based materials swelling can be observed due to the formation of Ni-Si compounds. The volume increase can be prevented and shrinkage can be observed if higher sintering temperatures (up to 1200°C) are applied. The strength of the alloys is increased by the addition of copper which is also visible for the Al-alloyed materials, especially with 6% Al. The mechanical properties of Si-alloyed materials can be improved by increasing sintering temperature.

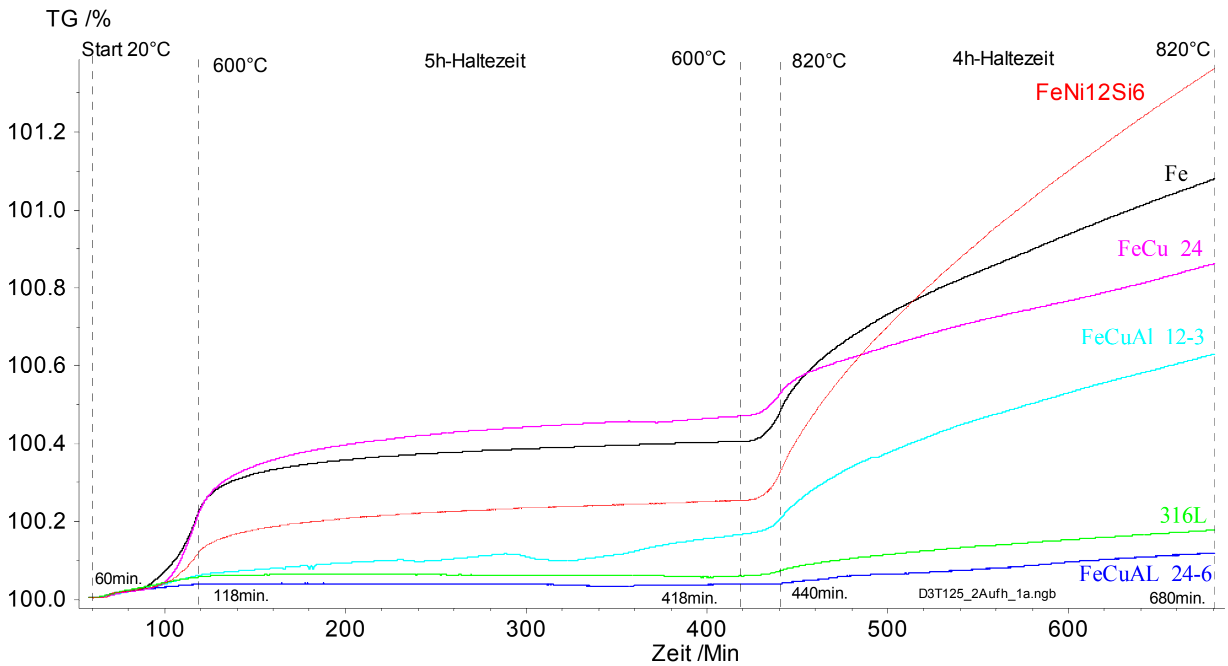

Fig. 8 TG measurements of different iron based alloys

Figure 8 displays the results of first tests of the oxidation behaviour of Al-alloyed and Si-alloyed iron based materials in comparison to conventional Fe, Fe-24Cu alloy and 316L as well. The weight change of the samples was measured up to temperatures of 820°C. This temperature is below the transformation temperature of iron and iron-copper as well. It can be seen that the addition of aluminium leads to an improved oxidation resistance resulting in a comparable oxidation behaviour with 316L if 6% Al are added. Addition of 3% Al is insufficient because it leads only to a small improvement of the oxidation resistance compared to pure iron and FeCu24. Furthermore the Si-alloyed iron based materials are shown comparable oxidation behaviour to pure iron and the Fe-Cu alloy. The reason could be that only an insufficient amount of silicon is available to form an protective oxide layer due to expected phase formations in the Fe-Si binary system during sintering.

Summary

Iron based materials alloyed with different amounts of aluminium and silicon can be prepared by a cost effective PM technology based on conventional press and sinter technology. Suitable pre-alloys CuAl and NiSi were added to iron powders and sintered under hydrogen. Tensile strengths of about 200MPa in combination with a ductility up to 2% can be achieved. Further improvements of the mechanical properties can be expected by reducing the porosity (higher compaction pressure, optimised sintering conditions).

The TG measurements clearly demonstrate the improved oxidation resistance of Al-alloyed iron based materials compared to iron and Fe-Cu alloys. The weight change during oxidation treatment is comparable with 316L alloy. Si-alloyed iron based materials have not shown considerably improved oxidation resistance up to now.

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