Cast iron alloys for exhaust applications

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Downsizing of engines – gasoline as well as Diesel - helps to reduce CO2-emissions. Smaller engines at the same or even raised power levels result in higher exhaust gas temperatures. In personal cars, these are raised to above 850°C in Diesel engines and up to 1,050 °C for turbocharged gasoline engines. Ferritic Si- and Mo-alloyed ductile iron grades are standardised in Europe in EN-16'124. However, these materials are not sufficient for highly turbo charged engines. Based on SiMo ductile iron, new ferritic materials have been developed to raise ferrite/austenite transition temperature, high temperature strength and scaling resistance. The paper describes the development of new ferritic high temperature ductile iron grades, their properties, serial applications and newest achievements in realizing even higher working temperatures.

Keywords: ductile iron, SiMo, temperature resistance, exhaust manifold, turbocharger, ferrite/austenite transformation.

Introduction

The omnipresent public discussion about climate warming and the required drastic reduction of CO2 emissions forces the car producers to develop new cars with lower gasoline consumption and reduced emissions as soon as possible. The raise of specific power and mean pressure of downsized engines leads to a raise of exhaust temperatures. These are in the region of 850 to 900 °C for Diesel engines. For turbocharged gasoline engines, a value of 1,050 °C is mentioned.[1]
Additionally, the downsizing concept leads to rising transferred energy amounts with respect to the cylinder volume.
These actual engine developments lead in summary to a remarkable increase of thermal demands of components which are in contact with exhaust gas such as exhaust manifolds or turbochargers. Conventional materials hit their limitations therefore and new solutions have to be found. In general, the component temperatures remain 50 to 80 °C below the exhaust gas temperature, but at exposed positions – e.g. thin walled areas in contact with exhaust gas from several sides, or areas with thermal insulation – the temperature of the material can reach values close to these of the exhaust gas.

Materials for exhaust applications

Depending on exhaust temperatures, various materials are used for these applications. For exhaust manifolds, welded steel sheet constructions are in competition with castings, while turbocharger housings are cast in almost all cases. Ferritic cast iron with 4 to 5 % Silicon and 0.5 – 1.0 % Mo, compacted graphite cast iron (GJV) as well as nodular iron (GJS) is used for component temperatures up to 820 °C. Along with standard SiMo materials, variants with additional Cr or Ni in the range of 0.5 to 1.0 % are available (SiMoCr and SiMoNi, respectively), which are said to have a higher scaling resistance. At higher exhaust temperatures up to 950 °C, either austenitic ductile iron grades, such as GJSA-XNiSiCr35-5-2, known also as Ni-Resist D5S, or highly Cr alloyed ferritic steels are used. At temperatures up to 1'000 °C or slightly higher, only highly alloyed austenitic steels are able to fulfil the requirements. At even higher temperatures, Ni-based alloys have to be used.

Superior grade materials often need a higher amount of alloying elements. Thus, material costs rise continuously with rising temperatures of the application. Especially Nickel, which exhibited a volatile market price in the near past, is used in large amounts. From an economic point of view, it is advantageous to develop lower alloyed and therefore cheaper materials to be used at elevated temperatures and to substitute more expensive materials

Because of these facts, we decided to further develop ferritic SiMo materials several years ago, and thus to extend the range of use of such material to higher temperatures. The aim of this development was to reach properties close to the austenitic ductile iron GJSA-XNiSiCr35-5-2, which is predominantly used at component temperatures of 820 °C up to 930 °C.

Requirements for materials for exhaust applications

Materials for exhaust manifolds and turbocharger housings are exposed to heavy thermal and thermo-mechanical loads. The most important properties of such materials are therefore: [2]

- Scaling resistance

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- Tensile strength, especially at elevated temperatures
- Temperature stability of the microstructure
- Thermal fatigue

Thermal fatigue or the resistance against thermo-mechanical fatigue are not singular material properties, but depend on various material characteristics. With each heating cycle of the component, temperature gradients are created which induce tension due to different thermal elongation at different positions and temperatures respectively. By mounting this component to another, such as the cylinder head, free thermal expansion is restrained, causing additional stress.

History of the development of ferritic ductile iron for temperatures above 800 °C

Si-Mo-alloyed ductile iron is known since more than 30 years – e.g., in 1980, Georg Fischer distributed documentation about such materials. [3] In the late 80s, French scientists did a lot of work to find a ductile iron material applicable at higher temperatures, adding some Aluminium. [4, 5] Due to massive problems caused by the very high tendency of this material to build oxide slags during the pouring process, the development was not successfully introduced on the market. We do not know an industrial application of this material. At the end of the 90s, we pursued the French work and developed the patented material 'SiMo1000®'. [6] In 2008, with further development of this material and especially the casting process, it was possible to go into serial production of exhaust manifolds and turbocharger housings for exhaust temperatures close to 900 °C:

Fig.1: Examples of a serial exhaust manifold and turbocharger housings made of GJS SiMo1000.

Further development of GJS SiMo materials

First experiments consisted of casting samples with various chemical compositions, measuring their ferrite/austenite transformation temperatures by dilatometry and evaluating the influence of the alloying elements on the transformation temperature. It could be shown that Molybdenum, Silicon and Aluminium increase the transformation temperature. The combination of Silicon and Aluminium by a Si-equivalent (Si-eq. = % Si + 0.8 x % Al) results in a much better correlation to the transformation temperature than with the two elements separately:

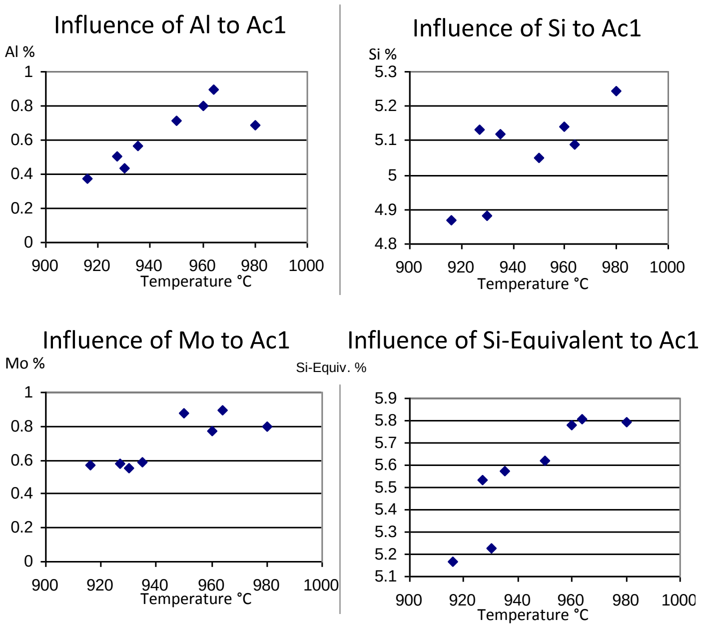


Fig.2: Influence of different alloying elements on the ferrite/austenite transformation temperature

Using multiple regression analysis, a formula to predict transformation temperatures was developed. A comparison of calculated and measured transformation temperatures is given in Fig. 3:

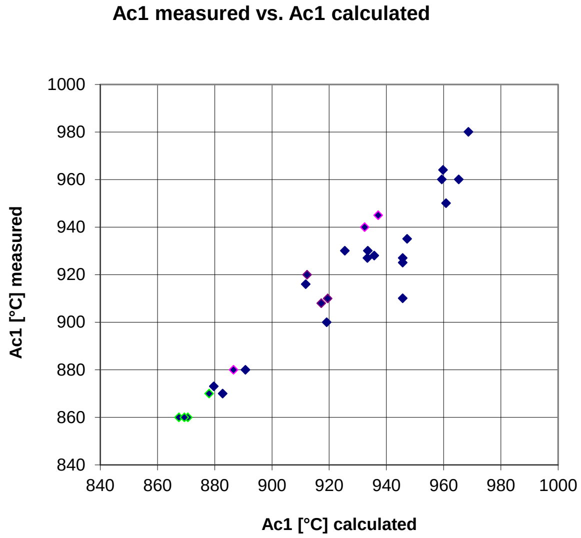


Fig.3: Correlation between calculated and measured ferrite/austenite transformation temperatures

However, a ferrite/austenite transformation temperature which is higher than the exhaust gas temperature is only one criterion for the applicability of a material. Furthermore, strength, creeping behaviour and scaling at elevated temperature have to be considered. Scaling still has to be improved by empirical trials by varying chemical composition and measuring the behaviour at elevated temperatures. Fig. 4 for example shows the scaling of different materials: compared to conventional materials, the GF SiMo 1000® exhibits a much better resistance to high temperature oxidation.

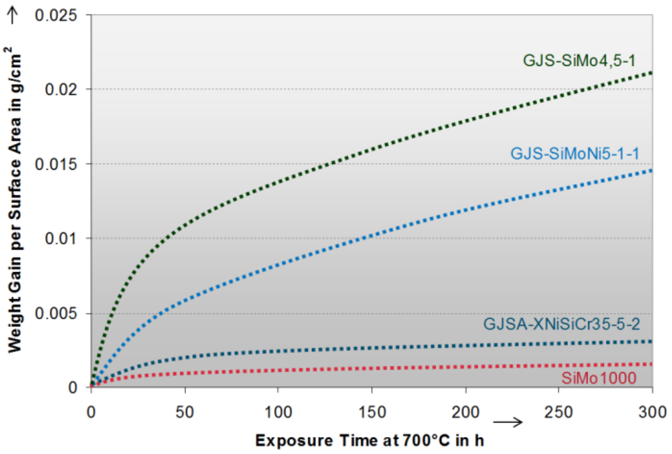


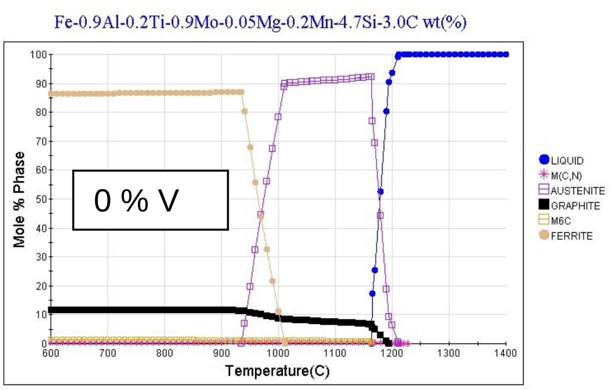
Fig.4: Scaling of different high temperature materials in unmoved air at 700 °C.

But for the prediction of transition temperature and possible precipitations and phases to improve high temperature strength and creeping, we do have simulation tools today.

Results and Discussion

Influence of Vanadium

Fig. 5 and 6 show a comparison of simulation results using the software JMatPro. Two chemical compositions with a variation of the Vanadium content were simulated, one without V, the other one with 0.4 wt-% V:



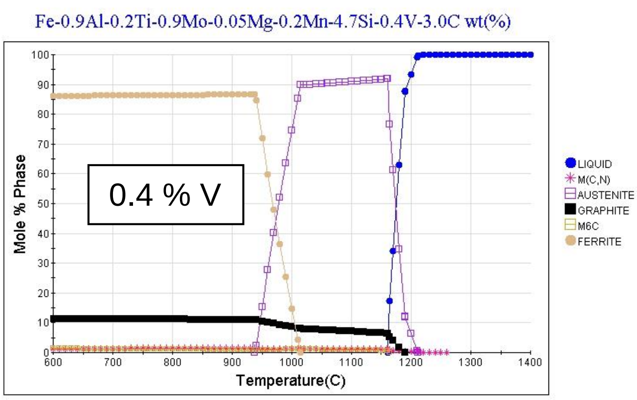
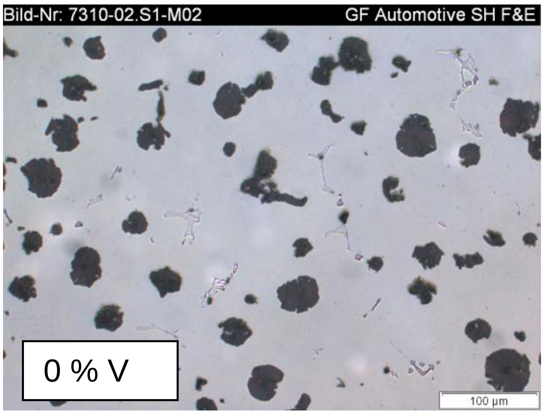


Fig.5(left) and 6 (right):
JMatPro-Simulation of two compositions with variations in the Vanadium content: Fig. 5 without, Fig. 6 with 0.4 % V. The simulation shows a ferrite/austenite transformation temperature of 935 °C without V and 938 °C with 0.4 % V. The addition of 0.4 % V leads to a raise of 0.42 % M(C, N) to 1.2 % and a drop of 2.21 % M6C to 0.86 %. M(C,N) consists of VC, where as M6C consists of Mo6C and Fe6C.

The experiment results in an increased total amount of carbides in the microstructure:



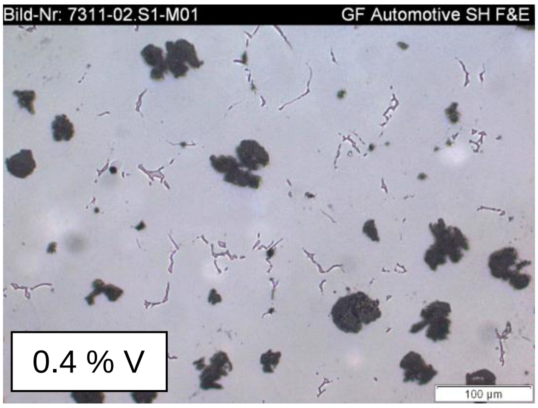


Fig.7(left) and 8 (right): Micrographs of the two variants without V (left) and with 0.4% V (right). The experiment confirms the predicted higher amount of carbides with 0.4 % V.

The effect of the higher carbide content was an increase of tensile strength at 800 °C from 52 MPa to 63 MPa (+20%).

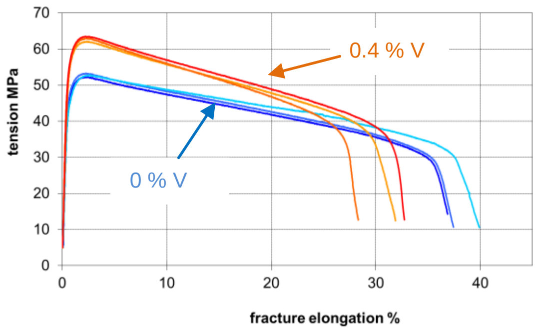


Fig.9: Result of tensile tests at 800 °C: significantly higher tensile strength with 0.4 % V (measured at ÖGI with a speed of 0.3 mm/min, according to ISO 6892-2:2011 .)

However, not every simulation result can be reproduced by experiment: According to the simulation, the variant with 0.4 % V should exhibit a ferrite/austenite transformation temperature of 938 °C, compared to 935 °C without V. The result of the experiment is shown in figure 10:

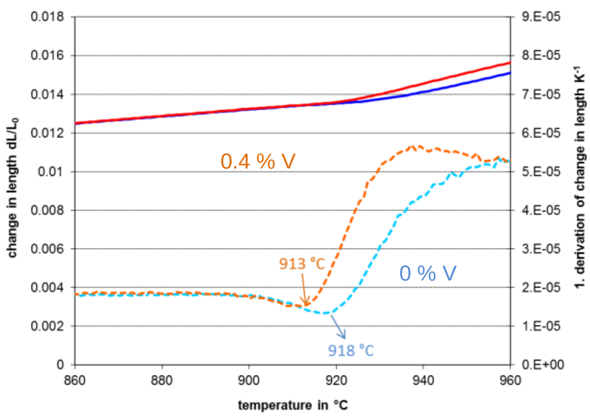


Fig.10: Result of measuring the ferrite/austenite transformation temperature by dilatometer.

The dilatometric measurement shows that 0.4 % V reduced the ferrite/austenite transformation temperature by 5 °C instead of increasing it by 3%. But both differences - simulation and experiment - are very small and can be interpreted as insignificant.

One limitation of simulation methods is the lack of data on some elements of interest, e.g. the solid solution strengthening element Co, which is known to raise transformation temperature and tensile strength at elevated temperatures.

Further Experiments

The element Cobalt is known as a ferrite stabilizer and a ferrite strengthener by solid solution. Adding Co to a SiMo iron could thus be a possibility to raise ferrite/austenite transformation temperature and high temperature strength. Unfortunately, our simulation tools have no Co implemented. To characterize the influence of Co, its effect on transformation temperature was measured empirically:

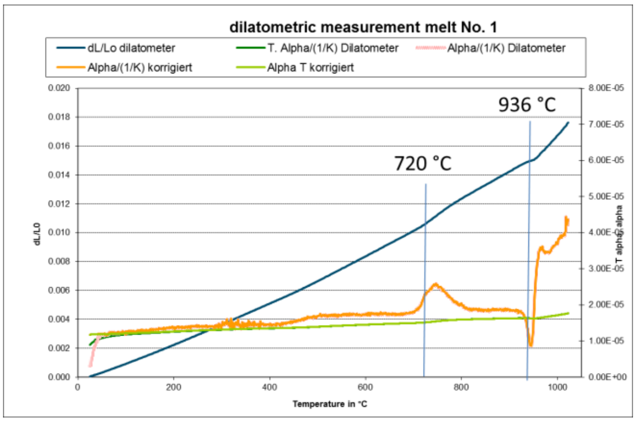
Melt No. 1 was prepared with the following composition:

2.5 % C, 5.2 % Si, 0.25 % Mn, 0.21 % Cu, 0.6 % Al, 1.8 % Co.

The composition of melt No. 2 was:

2.5 % C, 5.2 % Si, 0.24 % Mn, 0.21 % Cu, 0.4 % Al, 4.0 % Co.

Using our empirical formula the calculated ferrite/austenite transformation temperature was around 930 °C and 920 °C for melt No. 1 and melt No. 2, respectively (10% lower due to the influence of Al) – without considering Cobalt in the calculation.



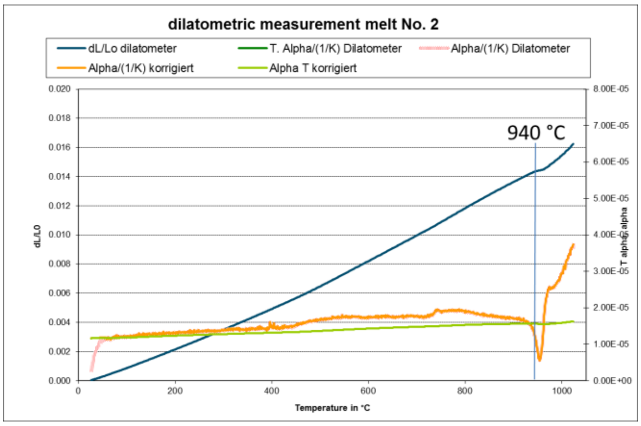
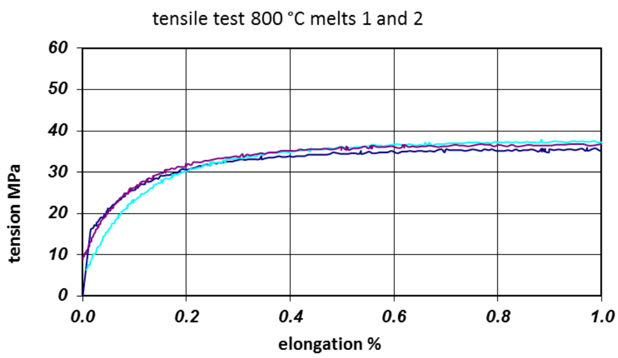


Fig.11 (left) and 12 (right): Dilatometry measurement graphs, indicating the ferrite/austenite-transformation temperature of melt No. 1 with 1.8 % Co, and melt No. 2 with 4.0 % Co. The first peak of melt No. 1 at 720 °C is probably due to solution of remaining pearlite.

The difference between calculated and measured transformation temperature is increased from plus 6 to plus 10 °C by raising the Cobalt content from 1.8 to 4.0 %. It seems therefore, that Co has a moderate raising effect on the transformation temperature. Considering the insignificant effect of Co on high temperature strength (see Fig. 13 and 14), the importance of this element as an alloy is negligible both from technological and commercial points of view.



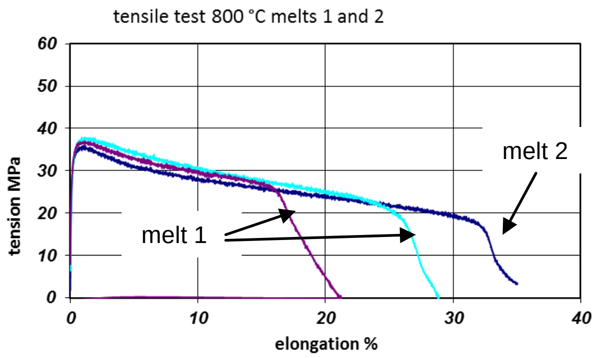


Fig.13 (left) and 14 (right): Result of tensile tests at 800 °C. The tensile strength Rm of melt No. 1 with 1.8 % Co and melt No. 2 with 4.0 % Co is 36 MPa and 38 MPa, respectively.

The next step was to raise the ferrite/austenite transformation temperature to values above 1,000 °C by increasing the Silicon and Aluminium contents compared to previous compositions and to serial production. Two further melts were thus prepared:

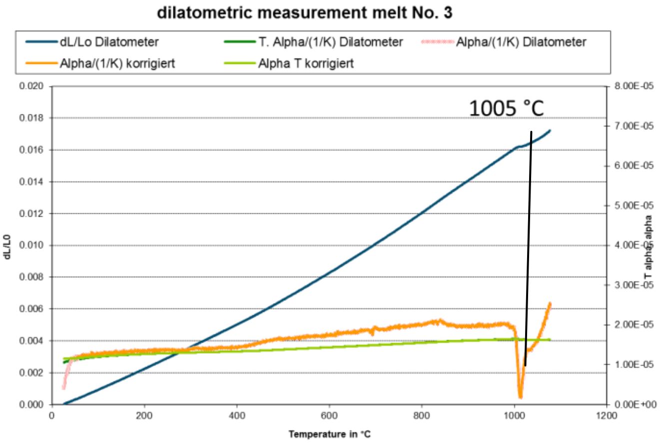
Melt No. 3 with the following composition:

2.5 % C, 5.3 % Si, 0.27 % Mn, 0.2 % Cu, 1.96 % Al, 0.15 % Cr, 0.42 % V, 1.8 % Co.

And melt No. 4 with:

2.5 % C, 5.5 % Si, 0.27 % Mn, 0.2 % Cu, 2.91 % Al, 0.15 % Cr, 0.40 % V, 1.7 % Co.

Using our empirical formula, the ferrite/austenite transformation temperatures were expected around 988 °C and 1,040 °C for melts No. 3 and No. 4, respectively (mainly due to the influence of Al) – again without considering Cobalt.



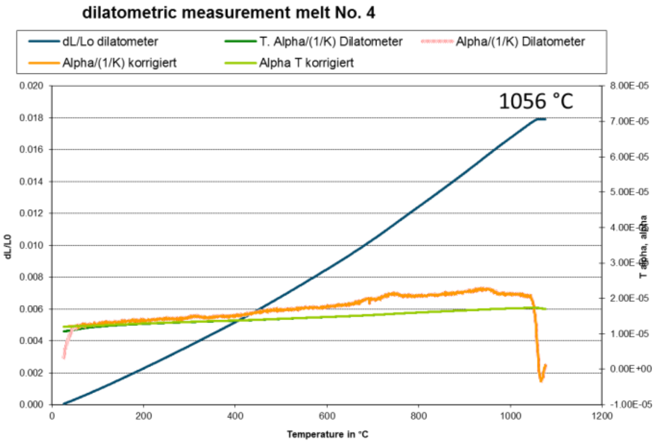
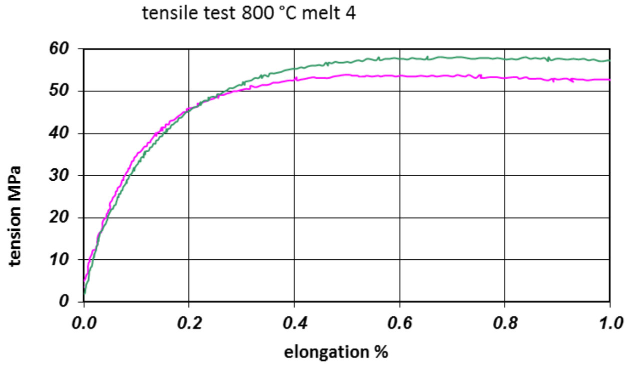


Fig.15 (left) and 16 (right): Dilatometry measurement graphs, indicating the ferrite/austenite transformation temperature of melt No. 3 with 5.3 % Si and 1.96 % Al, and melt No. 4 with 5.5 % Si and 2.91 % Al.

The dilatometer measurements confirm, that the influence of Cobalt on the transformation temperature is negligible, but that there is a significant influence of Silicon and Aluminium. With 5.5 % Si and 2.9 % Al, it is possible to attain transformation temperatures well above 1,000 °C. Tensile strengths at 800 °C were also increased, as depicted in Fig. 17 and 18:



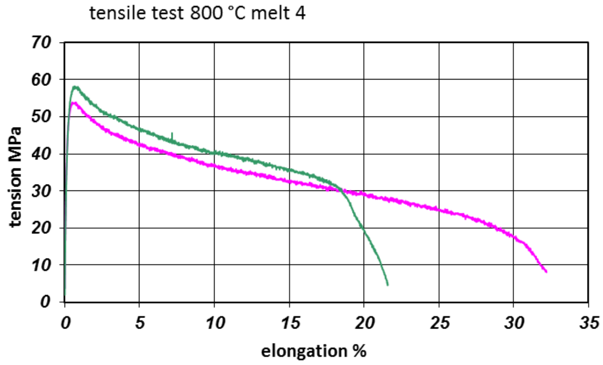


Fig.17 (left) and 18 (right): Result of two tensile tests of melt No. 4 with 5.5 % Si and 2.9 % Al at 800 °C. The tensile strength Rm is 54and 58 MPa (measured at GF central lab with a speed of 0.2 mm/min., according to ISO 6892-2:2011). No values of melt No. 3 available.

Conclusions

1. Downsizing of engines helps to reduce CO_2-emissions and is actually one of the most important goals of the automotive industry.
2. Downsizing of engines leads to higher exhaust gas temperatures and higher thermomechanical loads on exhaust systems. Conventional GJS SiMo cannot be used anymore for most actual engines.
3. In the late 80s, French researchers developed a Silicon and Aluminium alloyed ductile iron material for higher temperatures, but due to extreme oxidation of the melt during the casting process, no serial application was achieved.

4. At the end of the 90s, Georg Fischer pursued the idea and developed a new GJS SiMo material on the basis of the French idea. This material can be used at exhaust gas temperatures up to 900 °C, which is suitable for exhaust manifolds and turbocharger housings of downsized Diesel engines, but not enough for turbocharged gasoline engines.
5. Recent investigations on as-cast ductile iron materials with Cobalt as alloying element showed, that this element slightly raises the ferrite/austenite transformation temperature, but has no significant effect on high temperature strength. The price of Co is too high to see an advantage in using this element.
6. Therefore, ductile iron materials with increased Si-, Al-, Cr-, V-, Ti-, N-contents show a big potential for a new as cast ductile iron with moderately higher element costs compared to conventional SiMo, but with a ferrite/austenite transformation temperature above 1,000 °C and a high temperature strength similar to the much more expensive austenitic ductile iron. This new material provides a potential for being used for exhaust manifolds and turbocharger housings of charged gasoline engines.
7. According to the experience we made with the development of the GF SiMo 1000® material, we have to assume, that still a lot of work has to be done until this new material is optimized so far for industrial production.

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