# ELEVATED-TEMPERATURE MECHANICAL PROPERTIES OF SINTERED IRON-BASE MATERIALS CONTAINING CALCIUM FLUORIDE ADDITIONS

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In modern liquid-metal-cooled power plants there are mechanisms the friction units of which operate at elevated temperatures in contact with a liquid metal or metal vapor. The choice of bearing materials for such friction units must be based on comprehensive investigations involving determinations of frictional, physicomechanical, corrosion, and other properties. It has already been established that sintered iron-base materials with additions of a heat resistant solid lubricant (calcium fluoride) operate in a stable manner at elevated temperatures both under dry sliding friction conditions [1, 2] and in contact with liquid metals and metal vapors [3].

In the work described below a study was made of the mechanical properties (hardness and impact, transverse rupture, and compressive strengths) of sintered iron-base materials of optimum composition, containing 6 and 9 wt.% of calcium fluoride, and also of a similar material additionally alloyed with molybdenum (15 wt. %). The mechanical properties of these materials were determined at temperatures of up to 650°C, i.e., the maximum operating temperature of some bearing units of existing power plants. The dimensions of the specimens used in the tests and some of their properties are given in Table 1.

Compressive and transverse rupture strength measurements on sintered specimens in the temperature range investigated were made in air, using a BLW-30 hydraulic universal machine fitted with special attachments (for details of testing procedure and the designs of the attachments see [4]).

Impact strength determinations were made in a KM-0.5 machine, the design of which enables the energy stored in its pendulum for testing to be varied from 0.25 to 0.9 kg-m. The energy stored in the pendulum was 0.45 kg-m in tests on specimens of compositions $Fe_6CaF_2$, $Fe_9CaF_2$, and $Fe_{15}Mo_6CaF_2$ and 0.9 kg-m in tests on specimens of pure iron, a more ductile material. The distance between the supports was 32 mm. The specimens were heated up to the testing temperature in a resistance furnace provided with an argon atmosphere.

The hardness of the materials was measured with a UVT-2 tester (in a vacuum corresponding to $1 \cdot 10^{-5}$ mm Hg under a load of 1 kg applied for 60 sec), using a synthetic corundum single crystal as the indenter. The heating up of the specimens to the testing temperature was performed with a tungsten heating element. The design of the tester and the testing procedure are described in detail in [5]. The results of these tests are shown in Figs. 1-4.

From Fig. 1 it follows that the addition of 6% of calcium fluoride does not significantly alter the room-temperature hardness of sintered iron. With rise in testing temperature the hardness of both pure iron and materials containing calcium fluoride falls (Fig. 1). The higher hardness of $Fe_9CaF_2$ material at 20 and 200°C compared with pure iron and $Fe_6CaF_2$ is presumably attributable to the high concentration of calcium fluoride, whose microhardness (193.0-204 kg/mm$^2$) is 1.5-1.6 times that of the ferritic matrix of the material (111-129 kg/mm$^2$). At testing temperatures of 400 and 650°C the materials containing 6 and 9% of calcium fluoride were found to be less hard than pure iron. Clearly, at these temperatures $CaF_2$

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TABLE 1. Types of Tests and Properties of Materials Investigated

| Material comp., % | Type of test | Specimen dimensions, mm | Porosity, % | Brinell hardness HB, kg/mm² |
|---|---|---|---|---|
| Fe | Hardness | Diam. 8×5 | 8,0—10,0 | 50,0—52,4 |
| $Fe6CaF_2$ | | | 9,0—10,0 | 56,8 |
| $Fe9CaF_2$ | | | 4,0—6,0 | 62,4 |
| $Fe15Mo6CaF_2$ | | | 2,0—3,0 | 185 |
| Fe | Impact strength | 5×5×40 | 8,0—10,0 | 50,0—52,4 |
| $Fe6CaF_2$ | | | 9,0—10,0 | 56,8 |
| $Fe9CaF_2$ | | | 9,0—10,0 | 56,8 |
| $Fe15Mo6CaF_2$ | | | 2,0—3,0 | 185 |
| Fe | Compression | Diam. 10× 15 | 8,0—10,0 | 50,0—52,4 |
| $Fe6CaF_2$ | | | 8,0—10,0 | 56,8 |
| $Fe9CaF_2$ | | | 8,0—10,0 | 56,8 |
| $Fe15Mo6CaF_2$ | | | 6,0—8,0 | 168 |
| Fe | Transverse rupture | 7×7×70 | 8,0—10,0 | 50,0—52,4 |
| $Fe6CaF_2$ | | | 9,0—10,0 | 56,8 |
| $Fe9CaF_2$ | | | 9,0—10,0 | 56,8 |
| $Fe15Mo6CaF_2$ | | | 2,0—3,0 | 185 |

softens more than does an iron matrix, and this facilitates plastic deformation of the material. The alloying of iron with molybdenum raises the general level of strength in the temperature range investigated, thereby as a rule increasing its heat resistance [6]. Long-time (100-h) strength determinations made at 649°C on iron-base alloys with various amounts of molybdenum (up to 16%) revealed that their strength increased with rise in molybdenum content [6]. The optimum strength characteristics were found to be exhibited by alloys containing from 10 to 16% of molybdenum.

As can be seen from Fig. 1, the alloying of $Fe_6CaF_2$ material with molybdenum ensures a fairly high level of hardness in the temperature range investigated. With rise in temperature the hardness of $Fe_{15}Mo_6CaF_2$ material falls, from 240 kg/mm² at 20°C to 155 kg/mm² at 650°C, which is 8.6 times the hardness of pure iron at 650°C. In fact the hardness of $Fe_{15}Mo_6CaF_2$ material at 650°C is 1.6 times higher than the room-temperature hardness of pure iron (Fig. 1).

Compressive and transverse rupture tests on the materials in the temperature range investigated revealed that a molybdenum-containing material also possesses improved strength characteristics (Figs. 2 and 3). Now in compressive and transverse rupture tests pure iron specimens experienced a large strain with rupture (because of the high ductility of iron), and it therefore proved impossible to determine their limiting strength characteristics. In view of this, a comparison was made between the compressive and transverse rupture behavior of iron-base materials containing 6 and 9% of calcium fluoride and that of $Fe_{15}Mo_6CaF_2$ material. It was found (Figs. 2 and 3) that with rise in testing temperature the compressive and transverse rupture strengths of such materials falls, but in the case of a molybdenum-containing material the fall in strength is less steep, particularly at high testing temperatures.

The transverse rupture strengths of $Fe_6CaF_2$ and $Fe_9CaF_2$ materials at room temperature are 22.1 and 18.0 kg/mm², respectively, and are thus close to the strengths of existing ferrous bearing materials such as Zh20 and ZhGr1-20, which lie, depending on composition, in the range 18-26 kg/mm² [4]. Raising the testing temperature to 650°C decreases the transverse rupture strengths of $Fe_6CaF_2$ and $Fe_9CaF_2$ materials by factors of 2.8 and 2.5, respectively, compared with the room-temperature strengths, but alloying with molybdenum ensures a fairly stable level of strength in the temperature range investigated. Thus, $Fe_{15}Mo_6CaF_2$ material has a transverse rupture strength of 67.3 kg/mm² at room temperature and 57.2 kg/mm² at 650°C – values exceeding the corresponding values of strength of $Fe_6CaF_2$ material three and 7.4 times, respectively (Fig. 3).

Our impact tests demonstrated that the addition of calcium fluoride sharply lowers the impact strength of sintered iron (Fig. 4). Clearly, the effect of the nonductile calcium fluoride inclusions is similar to that of pores, and it is well known that the ductility of materials markedly decreases with increase in porosity [4, 7]. In the case of appreciable porosities (~30%) rupture usually occurs without any visible signs of permanent strain, even when the matrix of the material is of a ductile metal, such as iron.

From Fig. 4 it follows that with rise in testing temperature to 200°C the impact strengths of the materials investigated, like those of metals [8], increase. With further rise in testing temperature, right up

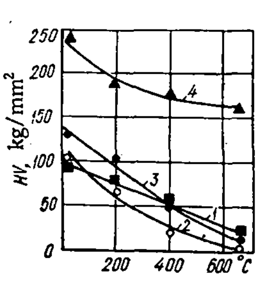

Fig. 1

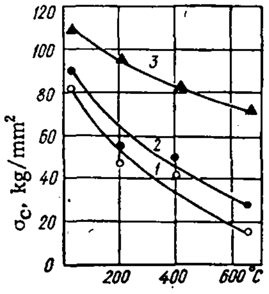

Fig. 2

Fig. 1. Variation of Vickers hardness HV with testing temperature: 1) Fe; 2) $Fe_6CaF_2$; 3) $Fe_9CaF_2$; 4) $Fe_{15}Mo_6CaF_2$.

Fig. 2. Variation of compressive strength $\sigma_c$ with testing temperature: 1) $Fe_6CaF_2$; 2) $Fe_9CaF_2$; 3) $Fe_{15}Mo_6CaF_2$.

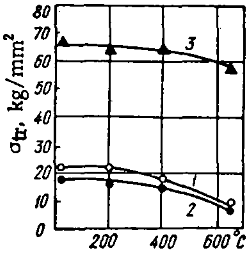

Fig. 3

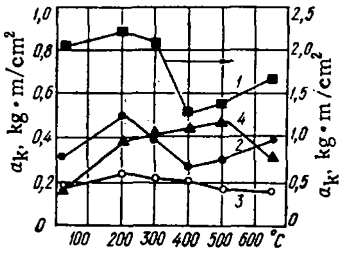

Fig. 4

Fig. 3. Variation of transverse rupture strength $\sigma_{tr}$ with testing temperature: 1) $Fe_6CaF_2$; 2) $Fe_9CaF_2$; 3) $Fe_{15}Mo_6CaF_2$.

Fig. 4. Variation of impact strength $a_k$ with testing temperature: 1) Fe; 2) $Fe_6CaF_2$; 3) $Fe_9CaF_2$; 4) $Fe_{15}Mo_6CaF_2$.

to 400°C, the impact strengths of iron and $Fe_6CaF_2$ and $Fe_9CaF_2$ materials decrease. With cast Armco iron such a fall in impact strength at elevated temperatures has been referred to as "blue brittleness." According to [8] the phenomenon, whose physical nature is identical with that of aging, involves the precipitation of certain components in very finely divided form out of a solid solution. These components are probably oxides, carbides, and nitrides. For Armco iron the blue brittleness temperature range extends from 350 to 450°C.

In tests on sintered iron and $Fe_6CaF_2$ material the smallest values of impact strength were recorded at 400°C (Fig. 4). This finding is in accord with data reported in [8]. For $Fe_9CaF_2$ material the temperature dependence of impact strength has a rather different character. The variation of its impact strength with temperature in the range investigated is very slight, from 0.24 to 0.16 kg-m/cm², which is due to a substantial weakening of the metallic skeleton by the nonductile calcium fluoride addition. Bearing in mind that calcium fluoride inclusions act as pores and taking into account the true porosity of the sintered specimens used in this work (Table 1), the "total porosity" of the material was found to be 28.0-30.0%. As noted above, such a level of porosity would be expected to have a marked deleterious effect upon ductility. As a result of this, the rupture of $Fe_9CaF_2$ specimens occurred without any visible signs of permanent strain, and consequently it proved impossible to determine the range of blue brittleness for this material.

With rise in temperature the impact strength of $Fe_{15}Mo_6CaF_2$ material at first increases, reaching its maximum value ($a_k$ = 0.47 kg-m/cm²) at 500°C. As the temperature is further raised to 650°C, the impact strength decreases, but is still twice as high as the initial strength. The increase in impact strength in the temperature range up to 500°C is attributable to certain structural changes taking place in the material during heating. Metallographic and x-ray structural studies demonstrated that in the as-sintered condition

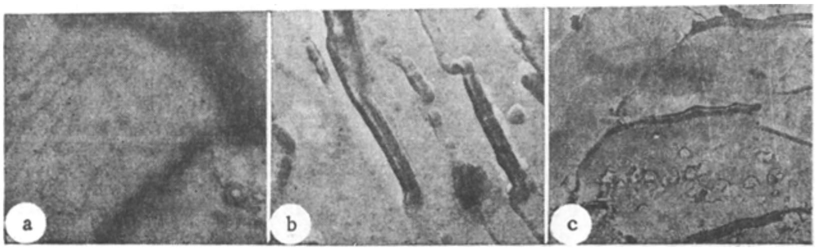

Fig. 5. Fractograms of $Fe_{15}Mo_6CaF_2$ specimens ruptured in impact tests at temperatures of 20 (a and b) and 400°C (c). Magnification: a) × 1000; b) × 16,000; c) × 5000.

the matrix of $Fe_{15}Mo_6CaF_2$ material is a supersaturated $\alpha$ solid solution with precipitated $\varepsilon$ phase particles, located both in the grains and at their boundaries. During heating the molybdenum in the material may migrate from the grain boundaries into the grains, bringing about an increase in impact strength. Metallographic examinations of microstructures of $Fe_{15}Mo_6CaF_2$ specimens preserved by quenching in water from testing temperatures established that raising the testing temperature to 500°C substantially alters the condition of the grain boundaries. In the initial condition the $\varepsilon$ phase forms a continuous network of particles distributed along the grain boundaries, while at 500°C the particles precipitated at the grain boundaries are fewer in number and less thick. A specimen of the material tested at 500°C contains the bulk of its $\varepsilon$ phase in its grains, and consequently experiences maximum strengthening (Fig. 4). The structure of a specimen tested at 650°C differs only slightly from that observed at 500°C, and the fall in impact strength at 650°C is evidently due to a general decrease in the heat resistance of the material.

The microhardness of the matrix of $Fe_{15}Mo_6CaF_2$ material was found to rise from 310 $kg/mm^2$ in the as-sintered condition to 470 $kg/mm^2$ at a temperature of 650°C. This rise, too, was due to the above-described processes of $\varepsilon$ phase precipitation from the supersaturated $\alpha$ solid solution.

In the temperature range investigated specimens of $Fe_{15}Mo_6CaF_2$ material ruptured in a brittle manner, showing no signs of permanent strain. Examination, under a Neophot optical microscope, of the fracture surfaces of specimens used in room-temperature impact tests (Fig. 5a) revealed that their rupture had a brittle intergranular character. Now, depending on the nature of the initiators inducing it, brittle intergranular rupture can be of one of the following two types: rupture in which there are films of a precipitated brittle phase at the grain boundaries and rupture in which the grain boundaries are embrittled by segregation of impurities alone, without the appearance of a separate phase [9, 10]. The presence in the structure of $Fe_{15}Mo_6CaF_2$ material of precipitates of the brittle $\varepsilon$ phase along the grain boundaries indicates that rupture in this case is of the former type.

As can be seen from Fig. 5b and c, the facets of the fracture surfaces of impact-ruptured specimens were fairly smooth and made up of small steps, and thus revealed the characteristic "river pattern" of brittle rupture [11]. With this type of rupture, according to [9], the crack skirts brittle precipitates and propagates along ferritic-matrix/precipitate interfacial boundaries. Some typical areas on the fracture surfaces of specimens tested at 20 and 400°C were examined also in a Japanese-made JEM-120 electron microscope. Photographs were taken, using carbon replicas, at an accelerating voltage of 100 kV. The examination revealed that the fractures of specimens tested at 400°C (Fig. 5c), like those of specimens tested at 20°C (Fig. 5a and b), were quite smooth and closely followed grain surfaces. The presence of some $\varepsilon$ phase precipitates in the boundary zones of grains (Fig. 5b and c) apparently did not significantly hinder crack propagation. Thus, our fractographic study established that in the temperature range investigated the rupture of specimens of $Fe_{15}Mo_6CaF_2$ material has a brittle intergranular character. The energy expended in crack propagation in this type of rupture is, as is known from [10], much less than the corresponding energy needed for transgranular rupture. This explains why $Fe_{15}Mo_6CaF_2$ material possesses comparatively low impact strength.

In the light of what has been said above it may be concluded that $Fe_{15}Mo_6CaF_2$ material, which has been found to be superior in heat resistance to the other $CaF_2$-containing iron-base materials investigated, appears to show promise for operation at temperatures of up to 650°C in friction units which are not subjected to severe shock loads.

## CONCLUSIONS

1. It has been established that the alloying of sintered Fe–$CaF_2$ materials with molybdenum (15 wt.%) increases their hardness 2.5-8.6 times and raises their transverse rupture strength to 70-60 kg/$mm^2$ and their compressive strength to 110-70 kg/$mm^2$ at temperatures of up to 650°C.

2. Raising the $CaF_2$ content of sintered iron decreases its impact strength at temperatures of up to 650°C. It was found that for $Fe_6CaF_2$, $Fe_9CaF_2$, and Fe (porous) materials the variation of impact strength as a function of testing temperature is similar in character to that observed with cast Armco iron. The blue-brittleness range for sintered Fe–$CaF_2$ materials extends from 350 to 450°C.

3. It is shown that the impact strength of sintered $Fe_{15}Mo_6CaF_2$ material, unlike that of unalloyed materials, increases up to a temperature of 500°C as a result of migration of the molybdenum from the grain boundaries into the grains. In tests $Fe_{15}Mo_6CaF_2$ material cracks by a brittle intergranular rupture mechanism.

4. $Fe_{15}Mo_6CaF_2$ material surpasses in heat resistance all the other sintered $CaF_2$-containing iron-base materials investigated, and can therefore be recommended for operation at temperatures of up to 650°C in friction units which do not experience severe shock loads.

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