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Canadian Intellectual Property Office

CA 3024486 A1 2017/11/23

(21) 3 024 486

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2017/03/23
(87) Date publication PCT/PCT Publication Date: 2017/11/23
(85) Entrée phase nationale/National Entry: 2018/11/16
(86) N° demande PCT/PCT Application No.: EP 2017/056998
(87) N° publication PCT/PCT Publication No.: 2017/198377
(30) Priorité/Priority: 2016/05/19 (DE10 2016 109 254.1)

(51) Cl.Int./Int.Cl. *C04B 35/10* (2006.01), *C04B 35/101* (2006.01), *C04B 35/443* (2006.01), *C04B 35/626* (2006.01), *C04B 35/64* (2006.01), *C04B 35/66* (2006.01), *F27D 1/00* (2006.01)

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(54) Titre : GRANULATS DE SPINELLE IGNIFUGES CONVENANT POUR RENDRE ELASTIQUES DES PRODUITS IGNIFUGES EN CERAMIQUE GROSSIERE, PROCEDE POUR LES REALISER ET LEUR UTILISATION

(54) Title: SPINEL REFRACTORY GRANULATES WHICH ARE SUITABLE FOR ELASTICIZING HEAVY-CLAY REFRACTORY PRODUCTS, METHOD FOR THEIR PRODUCTION AND USE THEREOF

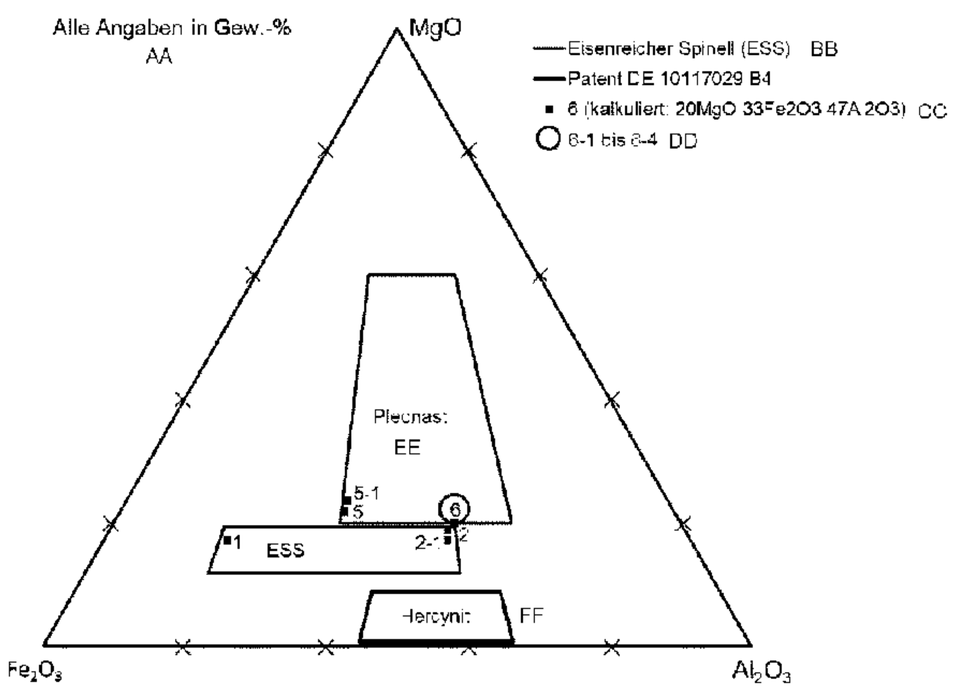

Fig. 1: System $MgO-Fe_2O_3-Al_2O_3$ (Darstellung in Gew.-%) mit dem beanspruchten Bereich der vorliegenden Erfindung (ESS) sowie des Patentes DE 10117029 B4 (Pleonast) und dem Bereich des Hercynit-Elastifizierers (DE 44 03 869 C2).

AA All indications in wt.-%
BB Iron-rich spinel (ESS)
CC 6 (calculated: 20MgO 33Fe2O3 47Al2O3)
DD 6-1 to 6-4
EE Pleonast
FF Hercynite
GG Fig. 1: System (MgO-Fe2O3-Al2O3 (shown in wt.-%) in the claimed range accord ng to the invention (ESS) and according to patent DE 10117029 B4 (pleonast) and the range of the hercynite elasticizer (DE 44 03 869 C2).

(57) Abrégé/Abstract:
The invention relates to a granular refractory mineral elasticizing granulate for refractory products, in particular for basic refractory products, wherein the minerals consist of mono-phase sintered spinel mixed crystals of the ternary system $MgO-Fe_2O_3-Al_2O_3$ of the composition range MgO: 12 to 19.5, in particular 15 to 17 wt.-%, remainder: Fe_2O_3 and Al_2O_3 in a quantity ratio range of Fe_2O_3 to Al_2O_2 between 80 to 20 and 40 to 60 wt.-%, the respective mixed crystals having an Fe_2O_3 and Al_2O_3 content, starting from an MgO content between 12 and 19.5 wt.-%, from the limited ranges indicated for each case, to obtain 100% in the total composition. The invention also relates to a method for producing said elasticizing granulate and to the use of the same.

Abstract

The invention relates to a granular, refractory mineral elasticizing granulate for refractory products, in particular for basic refractory products, wherein the minerals consist of mono-phased sintered spinel mixed crystal of the ternary system MgO-Fe_2O_3-Al_2O_3 of the composition range

MgO:	12 to 19.5, in particular 15 to 17 wt.-%,
Remainder:	Fe_2O_3 and Al_2O_3 in a quantity ratio range of Fe_2O_3 to Al_2O_3 between 80 to 20 and 40 to 60 wt.-%, wherein

starting from an MgO content between 12 and 19.5 wt.-%, the respective mixed crystals have an Fe_2O_3 and Al_2O_3 content in a solid solution out of the limited ranges respectively indicated therefore, such that a total composition of 100% is obtained. In addition, the invention relates to a method for production of the elasticizing granulate and to the use thereof.

Spinel Refractory Granulates Which Are Suitable For Elasticizing Heavy-Clay Refractory Products, Method For Their Production And Use Thereof

The invention relates to refractory spinel granulates which are suitable for elasticizing of coarse-ceramic, in particular basic, refractory products, to a method for production thereof and their use in coarse-ceramic, in particular basic refractory products containing spinel elasticizer.

Ceramic refractory products are based on refractory materials, e.g. on basic, refractory materials. Basic refractory materials are materials in which the sum of the oxides MgO and CaO clearly predominate. They are listed, for example, in tables 4.26 and 4.27 in the "Taschenbuch Feuerfeste Werkstoffe, Gerald Routschka, Hartmut Wuthnow, Vulkan-Verlag, 5th edition."

Elasticizing spinel granulates - hereinafter also called merely "spinel elasticizers" or "elastifiers" – which are usually employed in the form of coarse-grained granulates, are in a, e.g. basic, coarse-ceramic refractory product which comprises at least one refractory, mineral refractory material granulate as main component, these spinel granulates are refractory material granulates comprising a different mineral composition in comparison to the main component. The granulates are statistically distributed in the refractory product structure and elastify the structure of the refractory product by reducing the E- and G-modulus and/or by reducing the brittleness of the refractory product and thereby increase the resistance to temperature change or the resistance to temperature shock, for example due to formation of microcracks. Generally they determine the physical or mechanical and thermo-mechanical behavior of a basic refractory product which comprises as main component at least one granular, e.g. basic, refractory, mineral material. Elastifiers of this kind are, for example, MA-spinel, hercynite, galaxite, pleonaste, but also chromite, picrochromite. They are described, for instance, in section 4.2

of the handbook referenced above, in connection with various, for example basic, coarse-ceramic refractory products.

For example, standard granulations of granular spinel elastifiers are known to lie primarily between 0 and 4 mm, in particular between 1 and 3 mm. The granulations of the main component of the refractory products made from e.g. basic, refractory materials are known to lie primarily between 0 and 7 mm, and in particular between 0 and 4 mm, for example. The term “granular” is used hereinafter basically in contrast to the term meal or powder or meal fine” or “powdery”, wherein the terms meal or fines or finely divided are supposed to mean granulations of less than 1 mm, in particular less than 0.1 mm. Primarily means that every elastifier can comprise subordinated powder fractions and more coarse fractions. But also, every main component can contain meal or powder fractions up to e.g. 35 wt-%, in particular 20 wt-% and subordinated amounts of more coarse fractions. This is because we are dealing with industrially obtained products which can only be produced with limited accuracies.

Coarse-ceramic refractory products are primarily shaped and non-shaped, ceramically fired or non-fired products, which are obtained by a coarse-ceramic production method that uses grain sizes of the refractory components of e.g. up to 6 mm or 8 mm or 12 mm (Taschenbuch, page 21/22).

The refractory main component - also called the resistor - and/or the refractory main components of such e.g. basic refractory products, essentially guarantee the desired refractoriness and the mechanical and/or physical and chemical resistance, whereas the elastifiers, in addition to their elasticizing effect, likewise also support the mechanical and thermo-mechanical properties, but also possibly are provided to improve the corrosion resistance and also to enhance the chemical resistance to alkalis and salts, for instance. Generally the fraction of refractory main component predominates, that means it amounts to more than 50% by

mass in the refractory product, so that accordingly the content of elastifier generally lies in a range below 50% by mass.

Refractory elastifiers - also called microcrack-formers - are described for coarse-ceramic refractory products in DE 35 27 789 C3, DE 44 03 869 C2, DE101 17 026 B4, for example. Accordingly, these are refractory materials which increase the resistance of the structure of the refractory, e.g. basic, products to mechanical and thermo-mechanical stresses, in particular by reducing the E-modulus, and at least do not adversely affect the resistance to chemical attack, for example, to slag attack and to attack by salts and alkalis. As a rule, the causes for the elasticizing are disruptions in the lattice such as stress cracks and/or microcracks which make it possible that externally applied stresses can be dissipated.

It is known that basic refractory products containing aluminum oxide generally possess the sufficient mechanical and thermo-mechanical properties for their use e.g. in the cement, lime or dolomite industries at high operating temperatures around 1,500 °C. These products are commonly elastified by the addition of aluminum oxide and/or magnesium aluminate spinel (MA-spinel) to burnt magnesia or fused magnesia. Refractory products of this kind, based on magnesia, require low contents of calcium oxide (CaO), which is only possible through the use of well-processed, expensive raw materials. In the presence of calcium oxide, aluminum oxide and MA-spinel form fused $CaO\text{-}Al_2O_3$ and thus negatively affect the brittleness of the ceramic products.

In addition, in industrial furnace systems, for example, in cement kilns, at high temperatures reactions occur between aluminum oxide, in-situ spinel or MA-spinel and the fused cement clinker containing the CaO to produce minerals, e.g. Mayenite ($Ca_{12}Al_{14}O_{33}$) and/or Ye'elimite ($Ca_4Al_6O_{12}(SO_4)$), which can result in a premature wear of the furnace lining. In addition, dense and low-porosity magnesia spinel-stones which contain either sintered or molten MA-spinel (magnesium

aluminate spinel) as an elasticizing component, comprise a low tendency to form a stable deposited layer which forms on the refractory lining from fused cement clinker during operation and is desirable in the cement rotary kiln.

These disadvantages have led to the decision to employ hercynite ($FeAl_2O_4$) as an elastifier, namely in refractory products for the firing zones in cement rotary kilns, which products, due to the iron content of the elastifier, comprise a clearly improved crusting ability and in the case of synthetic hercynite (DE 44 03 869 C2) or iron oxide-aluminum oxide granulate (DE 101 17 026 A1), are added to the ceramic batch mass of the refractory products.

However, varying redox conditions which occur, for example, in the furnaces of the cement, dolomite, limestone and magnesite industries, in the case of hercynite-containing lining stones, lead to an adverse exchange of aluminum ions and iron ions at high temperatures. At temperatures above 800 °C a completely solid solution can take place within the material system of $FeAl_2O_4$ (hercynite)-Fe_3O_4 (magnetite) in the hercynite crystal, wherein below 800 °C a two-phase system with excreted magnetite forms, which causes an undesirable chemical and physical vulnerability of hercynite in refractory products under certain redox conditions.

The use of alternative fuels and raw materials in modern rotary furnaces, e.g. in the cement, limestone, dolomite or magnesite industry, results in considerable concentrations of alkalis and salts from various origins in their atmosphere. Hercynite is known to decompose at typical operating temperatures when exposed to oxygen and/or air to form $FeAlO_3$ and Al_2O_3. These multi-phased reaction products react with alkali compounds and salts to form additional secondary phases, which in turn, leads to an embrittlement of the refractory product and limits its use.

A multiple phase system of this kind also appears during the production of hercynite, during the sintering or fusing, namely due to oxidation during cooling. After cooling, a multi-phased product is present, with hercynite as main phase, and in addition, so-called secondary phases are also present. When using refractory products containing hercynite as an elastifier, that is, in situ in operating cement rotary kilns, for example, the production-related secondary phases also act like the secondary phases produced from hercynite at operating temperatures as described above, and have an embrittling effect.

To prevent the oxidation, it has been proposed according to CN 101 82 38 72 A to produce hercynite as a mono-phase, by carrying out the ceramic firing in a nitrogen atmosphere. But this method is very complicated and indeed can ensure a mono-phase of the hercynite, but this is nonetheless unstable in situ, and comprises a deficient resistance under oxidizing conditions in a furnace system.

The invention according to DE 101 17 026 B4 describes an alternative to the hercynite, in that as an elastifier, a synthetic refractory material of the pleonastic spinel type is proposed with the mixed crystal composition of (Mg^{2+}, Fe^{2+}) $(Al^{3+}, Fe^{3+})_2O_4$ and MgO-contents of 20 to 60 wt-%. In the literature, the continuous exchange of Mg^{2+}- and Fe^{2+}-ions in the transition from spinel sensu stricto (ss) $MgAl_2O_4$ toward hercynite ($FeAl_2O_4$) is described, wherein members of this series with Mg^{2+}/Fe^{2+}-ratios from 1 to 3 are designated as pleonaste (Deer et al., 1985 Introduction to the rock forming minerals). Compared to sintered or fused hercynite, these elastifiers comprise an improved resistance to alkali or clinker melts (Klischat et al., 2013, Smart refractory solution for stress-loaded rotary kilns, ZKG 66, pages 54-60).

In the case of the pleonaste resulting from the fusing or of the pleonastic spinels with 20-60 wt-% of MgO, the three mineral phases of $MgFe_2O_4$ss, $MgAl_2O_4$ and periclase are present, for example. The existence of these mineral phases re-

sults from an energy-intensive production process using components from the ternary system of MgO-Fe_2O_3-Al_2O_3 with disturbing secondary phases. Sintering and/or fusing in a smelting system, e.g. in an electric arc furnace, leads to a considerable quantity of secondary phases, such as FeO dissolved in MgO (MgOss, magnesiowüstite) and results in a complex mixture of several mineral phases.

DE 101 17 026 B4 describes that the modulus of elasticity (E-modulus) of examined refractory bricks is directly proportional to the increasing MgO content of the pleonastic spinel employed in them. An increase from 20 to 50 wt-% MgO in the examples caused an increase in the E-modulus from 25.1 to 28.6 GPa. The quantities of pleonastic spinel chosen here in many cases simultaneously cause the generation of mineral phases such as periclase (MgO), Magnesiowüstite (MgO ss) and Magnesioferrite ($MgFe_2O_3$), which - as inherent constituents - affect the expansion coefficient of the spinel and can have an adverse effect on the brittleness of the refractory product containing the spinel.

In determinations of ignition loss according to DIN EN ISO 26845:2008-06 at 1.025 °C, hercynite and pleonaste comprise an ignition gain of up to 4% or up to 2%, respectively. Under oxidizing conditions and at corresponding temperatures, the crystal lattice of hercynite decomposes. In the case of pleonaste, the Magnesiowüstite is converted into magnesioferrite.

The object of the invention is to create spinel elastifiers having a lower oxidation potential and/or being more oxidation-resistant, being better, and permanently more elastifying especially in basic refractory products, which elastifiers preferably provide in addition to the good elastifying properties, also a good thermochemical and thermo-mechanical resistance and a uniform elastifying ability at lower contents in comparison to the hercynite or pleonaste contents, for example - especially in basic refractory products, in particular when the refractory products containing them are used in cement rotary kilns, wherein they are furthermore

intended to cause a good crust formation. An additional object of the invention is to create coarse-ceramic, basic refractory products and uses for them, which are superior - due to their content of at least one elastifier granulate of the invented type - to the known coarse-ceramic, in particular basic, refractory products in regard to oxidation resistance and also in regard to thermo-chemical and thermo-mechanical resistance and crust formation in situ.

These objects are attained due to the features of claims 1, 7 and 12. Favorable refinements of the invention are characterized in the claims dependent on these aforementioned claims.

The invention also relates to elastifying spinel granulates produced by a sintering method in neutral, especially in oxidizing atmosphere, in particular in an air atmosphere, with compositions of the spinel selected in the ternary system of MgO-Fe_2O_3-Al_2O_3. The sintering method can be carried out much more efficiently in comparison to the fusing method. In addition the sintering method in comparison to the fusing method brings about the surprising effect, that an oxidation-resistant spinel mono-phase forms, which is resistant in situ and thus remains stable in a granulate containing coarse-ceramic refractory product, in particular in a basic refractory product containing at least one spinel elastifier according to the invention, and ensures the elastification and also the thermo-chemical and thermo-mechanical resistance of the product. In addition, the spinel mono-phase leads to a very good crust formation in a cement rotary kiln.

The existence of a region with spinel mono-phases in the form of complex ternary mixed crystals in the ternary system of MgO-Fe_2O_3-Al_2O_3 has been described by W. Kwestroo, in J. Inorg. Nucl. Chem., 1959, Vol. 9, pages 65 to 70, based on laboratory experiments. Thus, according to Figure 1 and 2 op. cit., a relatively large range of molecular weight was found in samples produced in air at firing temperatures of 1250 and 1400 °C and determined by x-ray analysis, in

which stabile spinel mono-phases of different composition are found to exist. It was determined therein that the magnetic saturation or the Curie temperature of the particular mono-phase can be a function of the chemical composition. Additional properties of the mono-phases were not investigated or stated. The mono-phases comprise different quantities of (Al, $Fe)_2O_3$ in solid solution in the spinel crystal.

Within the scope of the invention, in the ternary system of MgO-Fe_2O_3-Al_2O_3 a tight range of composition of mono-phased, stable mixed spinel crystal was found in the known, broad range of spinel mono-phases with mono-phased sintered spinel mixed crystals suitable as an elastifier, having the following composition according to the range in figure 1:

MgO:	12 to 19.5, in particular 15 to 17 wt.-%,
Remainder:	Fe_2O_3 and Al_2O_3 in a quantity ratio range of Fe_2O_3 to Al_2O_3 between 80 to 20 and 40 to 60 wt.-%.

The range of the ESS according to the invention is obtained as follows: The minimum and maximum MgO content was determined within the scope of the invention as 12 wt-% or 19.5 wt-%, respectively. The side bounds of the ESS-field are each lines of constant Fe_2O_3/Al_2O_3 ratios (wt-%).

Left bound: $Fe_2O_3/Al_2O_3 = 80/20$

Right bound: $Fe_2O_3/Al_2O_3 = 40/60$

Graphically speaking, these bounds represent a portion of the line connecting the peak of the triangle (MgO) to the base of the triangle. The relationships stated above are the coordinates of the points of the base of the triangle.

Starting from an MgO content between 12 and 19.5 wt.-%, the respective mixed crystals have an Fe_2O_3 and Al_2O_3 content in a solid solution, such that from the limited ranges indicated for each case, a total composition of 100 wt-% is obtained. Thus, with regard to MgO, the compositions always remain in the spinel range of the ternary system between 12 and 19.5 wt-% MgO.

Spinels from the invented range of composition which in granular form have bulk grain densities of at least 2.95, in particular of at least 2.99, preferably of at least 3.0 g/cm^3, especially of up to 3.2 g/cm^3, quite especially of up to 3.7 g/cm^3, measured according to DIN EN 993-18, are particularly suitable as an elastifier. These elastifiers have an optimum elastifying effect especially when mixed with coarse-ceramic, basic refractory products.

Within the sense of this invention, mono-phased means that in the technically produced mixed spinel crystals according to the invention, there are less than 5, in particular less than 2 wt-% of secondary phases, for example, originating from impurities in the starting materials.

It is an advantage if the grain compressive strength of the granules of the elastifier granulate lies between 20 MPa and 35 MPa, in particular between 25 MPa and 30 MPa (measured according to DIN EN 13005 - Appendix C). The granular spinel elastifiers according to the invention are produced and used preferably with the following grain distributions (determined by sieving):

0.5-1.0 mm 30-40 wt.-%

1.0-2.0 mm 50-60 wt.-%

In this regard up to 5 wt-% of granules smaller than 0.5 mm and larger than 2 mm can be present, which then reduce the quantities of the other granules accordingly.

The granules are used with the standard, usual grain distributions, in particular Gaussian grain distributions, or with particular, common grain fractions in which certain grain fractions are missing (gap grading), as is current practice.

The mono-phased sintered spinel elastifiers according to the invention can be unambiguously identified by means of x-ray diffraction as exclusively mono-phased, as will be explained below.

In addition, the spinel mono-phases can be analyzed as exclusively present in scanning electron microscopy images and quantitatively the composition of the mixed crystals and/or mono-phases can be determined with an x-ray fluorescence elemental analysis, e.g. with an x-ray fluorescence spectrometer, for example, using the Bruker model S8 Tiger.

Fig. 1 shows the range of composition found in wt-% for the mono-phased spinel mixed crystals suitable as elastifiers according to the invention, as an ESS bounded quadrilateral within the ternary system of MgO-Fe_2O_3-Al_2O_3, whereas the range of composition of the known pleonastic spinel elastifier is indicated as a pleonaste-bounded rectangle. In addition, the typical spinel elastifier composition of the normally used hercynite is indicated as a hercynite-bounded rectangle on the Fe_2O_3-Al_2O_3 composition line of the ternary system.

Thus the invention relates to iron-rich sintered spinels which lie within the ternary system of MgO-Fe_2O_3-Al_2O_3 and which are not assigned either to the hercynite spinels or to those of the pleonaste group. After sintering of the corresponding, high-purity raw materials or starting materials, the particular spinel product consists merely of a synthetic mineral mono-phase, and due to the predominance of the trivalent iron (Fe^{3+}) it displays little or no oxidation potential. Reactive secondary phases like those frequently encountered in pleonastic or hercynitic spinel types, for example, are not present or are not detected under x-ray, and cannot

impact the performance of refractory products containing the inventive spinel products.

If spinels according to the invention are used as elastifying components, even in small amounts, in shaped and non-shaped, in particular basic refractory materials, such as for furnace systems in the cement and limestone or dolomite industry or magnesite industry, then, when standard production methods are used, ceramic refractory products are obtained with a high corrosion resistance to alkalis and salts occurring in the furnace atmosphere. In addition, these refractory products display outstanding thermo-chemical and thermo-mechanical properties and also a strong tendency toward crust formation in the aforementioned industrial furnace systems at high temperatures, whereby the latter properties are probably attributable to relatively high, near-surface iron oxide contents of the refractory product.

According to the invention, spinel granulates that can be used as an elastifiers are found in a limited ternary system that brings in all advantages of chemical resistance, ready crust formation, elasticizing and also a good energy balance due to an economical production method for the refractory material. Thus, the invention closes a gap between hercynite- and pleonaste-spinel elastifiers, without having to deal with the disadvantages of the one or the other.

The mono phase spinels, which are used according to the invention in a granulate form and originating from the ternary material system of MgO-Fe_2O_3-Al_2O_3 differ essentially from the pleonastic spinels due to the valence of the cations and due to a lower MgO content. A magnesium excess which occurs only in the high-temperature range, does not appear in the ternary system of iron-rich spinel used according to the invention, the latter consists solely of a mineral mono-phase due to the absence of secondary phases such as, for example, magnesio-ferrite, Magnesiowüstite. Therefore, the mono-phased spinels used according to

the invention are superior to the pleonastic spinels because the named secondary phases are missing, which comprise coefficients of (longitudinal) expansion which are close to those of magnesia and thus have only a small elastifying effect.

The ecological and economical advantage is that the spinels used according to the invention can be produced by a simple method, which requires, after processing of three raw material components, a sintering process at moderate temperatures in comparison to fusing processes. Within the scope of the invention it was found that from a mixture of sintered magnesia, for example, naturally occurring iron oxide and/or mill scale as well as aluminum oxide will form a mineral mono-phase after sintering, wherein caustic magnesia, fused magnesia and metallurgic bauxite can also be used as starting materials.

The structural singularity of the invented spinels used as granulate makes it possible to incorporate oxides such as Al_2O_3 and/or Fe_2O_3 in solid solution into the crystal, such that the terminal elements are represented by γ-Al_2O_3 and/or γ-Fe_2O_3, respectively. This circumstance allows the production of the mineral mono-phase in the ternary, ternary system of MgO-Fe_2O_3-Al_2O_3, whose electrical neutrality is ensured due to cation voids in the spinel crystalline lattice.

In general, the difference in the expansion coefficient α of two or more components in a ceramic refractory product after its cooling after a sintering process, leads to the formation of micro-cracks primarily along the grain boundaries, and thus increases its ductility and/or reduces its brittleness, respectively. The mixing, shaping and sintering of burnt magnesia in the mixture with the spinel granulates according to the invention under application of common methods of production yields basic refractory materials with reduced brittleness, high ductility and outstanding alkali resistance, which is particularly superior to basic products which contain sintered or fused hercynite or sintered or fused pleonaste as an elastifier

component. In contact with the fused cement clinker phases in the cement furnace, the iron-rich surface of the invented refractory products containing the spinel granulate according to the invention, causes the formation of brownmillerite, which melts at 1395 °C, which contributes to a very good crust formation and thus to a very good protection of the refractory material against thermo-mechanical stresses due to the furnace charge in the furnace.

The production of the sintered spinel used as an elastifier according to the invention is described below as an example. As was already explained above, it pertains to an iron-rich sintered spinel from the composition range of ESS according to figure 1 in the ternary system of MgO-Fe_2O_3-Al_2O_3 (the sintered spinel is hereinafter briefly called ESS).

The starting materials are at least one magnesia component, at least one iron oxide component and at least one aluminum oxide component.

The magnesia component is in particular a high purity MgO component and in particular fused magnesia and/or sintered magnesia and/or caustic magnesia.

The MgO content of the magnesia component is in particular greater than 96, preferably greater than 98 wt-%.

The iron oxide component is in particular a high purity Fe_2O_3-component and in particular, natural or processed magnetite and/or hematite and/or mill scale, a byproduct of iron and steel production.

The Fe_2O_3-content of the iron oxide component is in particular greater than 90, preferably greater than 95 wt-%.

The aluminum oxide component is in particular a high purity Al_2O_3 -component and in particular, alpha and/or gamma alumina.

The Al_2O_3-content of the aluminum oxide component is in particular greater than 98, preferably greater than 99 wt-%.

These starting materials have preferably a meal fineness with grain sizes of ≤ 1, in particular ≤ 0.5 mm. They are thoroughly mixed until a homogeneous to nearly homogeneous distribution of the starting materials in the mixture is obtained. It is expedient to mix the meals in a grinding machine and to apply with a grinding energy that increases the fineness and as a result increases the reactivity of the meal particles for a sintering process. For example, the grinding and/or mixing can take place in a ball mill or roll mill which receives, for example, a ton of grinding stock within for example 20 to 40 minutes. Using simple grinding-mixing experiments, an optimization of the grinding-mixing process for reaction activation of the starting materials for the sintering process can be achieved. Grinding time can be, for example, 15 to 30 minutes, especially 20 to 25 minutes.

The meal fineness and mixing of the starting materials optimum for the sintering reaction can also be produced advantageously by grinding in a grinding machine, in that at least one granular starting material with grain sizes e.g. greater than 1, for example, 1 to 6 mm, is used, which is ground down into a meal during the grinding.

After the mixing/grinding, the fineness of the mixture should be, for example, 90 wt.-% <100 µm, especially <45 µm.

The mixing of the starting materials is then sintered, in a neutral or oxidizing atmosphere, especially with aeration, for example for 3 to 8 hours, especially 4 to 6 hours for example at temperatures between 1200°C and 1700°C, especially between 1450 and 1550°C, until the desired mono phase is achieved, wherein an ESS-solid body is formed or several solid bodies are formed. Next, the material is cooled and the solid body is crushed, for example, with cone or roller crushers or similar crushing systems, so that crushed granulates are formed that can be

used as an elastifier. Finally, the crushed, grainy material divided, for example, by screening, into specific ESS grain fractions. Rotary kilns, bogie hearths, shaft or tunnel furnaces can be used for the sintering.

Compaction of the mixture before sintering, for example by granulating, pressing, or vibrating, is advisable. Preferably compacted, especially pressed, shaped bodies such as tablets, briquettes, spherical or angular shaped bodies are produced from the mixture. The granules prefarably have a volume between 10 and 20 cm^3, especially between 12 and 15 cm^3, and bulk densities between 2.90 and 3.20 g/cm^3, especially between 3.00 and 3.10 g/cm^3. The bulk density is determined according to DIN EN 993-18. Pressed shaped bodies have volumes of, for example, between 1600 and 2000 cm^3.

The compressing of the mixture accelerates the sintering reactions and promotes the absence of secondary phases from the achievable monophases of ESS.

After sintering and cooling, when viewed mineralogically, in the respective mono phase, mixed crystals with Fe_2O_3 being in solid solution are present, wherein the iron preferably is present exclusively or at least for 90, especially at least for 95 mol.% in the trivalent oxidation state Fe^{3+}. In contrast thereto, in the case of a synthesis method with mixtures from the invented range via fusing, generally non-negligible amounts of bivalent iron Fe^{2+} as well as undesired mineral secondary phases are present.

For clear differentiation of the invention compared with pleonastic spinels according to DE 101 17 029 B4, mixtures of various compositions have been prepared as examples, using a method according to the invention as described above, each with the same starting materials and the same process, whose compositions are characterized by the points plotted in the limited fields of Fig. 1.

The compositions at the points 1, 2, 2-1 correspond to compositions of ESS for the invention (subsequently referred to also as “inventive composition” or “inventive spinel” or “inventive range”). The compositions at points 5, 5-1, as well as the points 6-1, 6-2, 6-3, and 6-4 which lie at “6” in the drawn circle, correspond to pleonastic compositions according to DE 101 17 029 B4.

The chemical composition at the respective points is as follows:

Compositions [wt.-%]	MgO	Fe_2O_3	Al_2O_3	SiO_2	Ignition loss [%]
1	17.49	63.33	17.37	0.80	0.14
2	17.64	33.02	48.22	0.40	0.19
2-1	19.41	32.06	47.42	0.37	0.11
5	21.42	46.49	30.65	0.57	0.22
5-1	25.26	44.64	28.60	0.63	0.03
6-1	21.01	32.54	45.30	0.38	0.12
6-2	25.86	30.37	43.69	0.26	0.03
6-3	21.29	32.27	45.34	0.35	0.12
6-4	22.26	31.73	44.91	0.35	0.17

Starting materials were an iron ore concentrate (magnetite) as well as high-quality fused magnesia and alumina. The sum of the oxides MgO, Fe_2O_3, and Al_2O_3 was 98 wt.-%. The following table contains the chemical analysis of the powdered starting materials in wt.-%.

	Magne-sia	Alumina	Magnetite		Total sample
SiO_2	0.09		0.8		0.27
Al_2O_3	0.08	99.5	0.28		48.06
Fe_2O_3	0.49		101.14		32.06
CaO	0.81		0.02		0.23
MgO	98.33				19.86

The weighed starting materials were ground and mixed for 4 minutes in a disk vibrating mill at 1000 RPM, wherein the resulting grinding stock had a fineness of < 45 µm. Subsequently it was moistened with denatured alcohol and the gridning stock was pressed into tablets with a diameter of 2.54 cm and a thickness of 1 cm (5.1 cm^3). After drying at 100°C, these tablets were fired for 12 hours at 1250°C in an electric furnace in an air atmosphere. Then the fired tablets were ground and samples were prepared for microscopic examination and phase analysis by means of X-ray powder diffraction.

Of the several criteria differentiating the iron-rich inventive spinel from the pleonastic spinel according to DE 101 17 029 B4, the monophasic nature, which can be illustrated by means of X-ray powder diffraction or reflected-light microscopy,

presents a characteristic feature. Fig. 2 shows X-ray diffractograms of the compositions 1, 2, 5, and 6-2 arranged vertically with one another. In the case of compositions 1 and 2, all reflexes can be assigned to a singular ESS mineral phase, i.e. ESS monophase, while compositions 5 and 6-2 clearly comprise at least a second crystalline mineral phase. As the X-ray diffraction images were taken with the same parameters, it can be clearly seen from the peak height and peak configuration that a multiphase is present in the case of compositions 5 and 6-2, while the images of compositions 1 and 2 clearly show a single phase.

Figures 3 to 6 show reflected-light microscopy images of the compositions 1, 2, 5, and 6-2. The images in Fig. 3 and 4 show only the spinel monophase “S” of the compositions 1 and 2 from the inventive sintered spinel range of the ternary system MgO, Fe_2O_3, Al_2O_3. The images in Fig. 5 and 6 show the spinel phase “S1” as the main phase and, to a lesser extent, the spinel phase “S2”. Thus there is not existing an exclusive monophase.

An X-ray powder diffractometer from the company Panalytical X’Pert Pro with an X’Cellerator Detector was used. The measurements were taken with a copper X-ray tube, with the excitation of the X-ray tube at 45 kV and 40 mA.

The oxidation resistance of the invented ESS is shown in Fig. 7a and 7b. Figure 7a shows the X-ray diffractogram after the production of an ESS with composition 1. Figure 7b shows the X-ray diffractogram after treatment of the ESS at 1250°C and 12 hours in an air atmosphere in an electric furnace. It can be seen that the original spinel structure remains intact despite temperature effects and the presence of oxygen. A new formation of mineral phases could not be determined by means of X-ray powder diffraction.

For comparison, a hercynite sample according to DE 44 03 869 A1 was melted and an X-ray diffractogram created (Fig. 8a). Afterwards, the hercynite sample was also treated at 1250°C for 12 hours in an electric furnace in an air atmos-

phere. The result is shown in Fig. 8b. It is clearly evident that the original spinel structure was disrupted by the temperature effects and oxidation of the bivalent iron (Fe^{2+}). The bivalent cations necessary for the crystal lattice of the hercynite spinel are no longer available. The newly formed phases are hematite (Fe_2O_3) and corundum (Al_2O_3).

The invention also pertains to the production of basic refractory products, for example basic refractory shaped bodies and basic refractory masses. For example, basic refractory products according to the invention comprise the following composition:

50 to 95 wt.-%, especially 60 to 90 wt.-% of at least one granular basic refractory material, especially magnesia, especially fused magnesia and/or sintered magnesia with grain sizes, for example, between 1 and 7, especially between 1 and 4 mm,

0 to 20 wt.-%, especially 2 to 18 wt.-% of at least one powdery basic refractory material, especially magnesia, especially fused magnesia and/or sintered magnesia with grain sizes ≤ 1 mm, especially ≤ 0.1 mm,

5 to 20 wt.-%, especially 6 to 15 wt.-% of at least one granular ESS according to the invention with grain sizes, for example, between 0.5 and 4, especially between 1 and 3 mm,

0 to 5, especially 1 to 5 wt.-% of at least one powdery ESS according to the invention as an admixture with grain sizes ≤ 1 mm, especially ≤ 0.1 mm,

0 to 5, especially 1 to 2 wt.-% of at least one binding agent known for use in refractory products, especially at least one organic binding agent such as lignin sulfonate, dextrin, methylcellulose.

Which binding agents are usable for which refractory products can be found in the aforementioned handbook, pages 28-29.

The following example shows that refractory products according to the invention, which have lower added amounts of elastifiers in comparison to added amounts with hercynite or pleonaste, can still achieve very good solid matter properties. The example composition was as follows:

43.1 wt.-% of sintered magnesia with grain sizes between 1 and 4 mm,

44.4 wt.-% of sintered magnesia meal with grain sizes under 1 mm,

10.5 wt.-% of ESS with composition 1 with grain sizes between 1 and 3 mm,

2 wt.-% organic binding agent.

Bricks were pressed from this mixture with a pressing force of 180 MPa, which were fired in a tunnel furnace in an air atmosphere at 1520°C for 6 hours.

The chemical composition of the fired refractory product is shown in the following table:

Oxide	[wt.-%]
SiO_2	0.8
Al_2O_3	5.0
Fe_2O_3	4.7
CaO	1.4
MgO	87.9

The physical and thermochemical properties are shown in the following table:

Bulk density, fired product [g/cm^3]	2.95
E modulus [GPa]	24.5
Cold compression strength [MPa]	75.8
Porosity [vol. %]	16.2
Thermal shock resistance at 1200°C [cracks, spalling, cycles]	3/-/>30
Refractoriness under load [$T_{0,5}$°C]	>1,700

With the same composition under the same treatment, a sample with a pleonaste granulate was created with the composition 6-2 of the spinel as an elastifier, instead of the ESS elastifier. The fired sample comprised a significantly higher E modulus, which is shown in the following table:

Bulk density, fired product [g/cm^3]	2.98
E modulus [GPa]	27.6
Cold crushing strength [MPa]	86.3
Porosity [vol. %]	14.7
Thermal shock resistance at 1200°C [cracks, spalling, breakage]	2/5/7
Refractoriness under load [$T_{0,5}$°C]	>1,700

The results of the example above show that with a lower amount of ESS elastifiers, E moduli can be achieved which are only possible with pleonaste as an elastifier if a markedly greater amount is added.

By means of basic magnesia shaped bodies which contain ESS, it will be shown below that these refractory products are more alkali-resistant than the same refractory products with hercynite spinel granulate or pleonaste spinel granulate.

Therefore, a test was run using the crucible method at 1400°C (residence time 3 hours) with potassium carbonate as a reaction agent. The test was carried out according to the method “Test Methods for Dense Refractory Products - Guidelines for Examination of Fluid-Induced Corrosion of Refractory Products; German Edition, CEN/TS 15418: 2006”.

The result is shown in Fig. 9. Compared to the “hercynite sample” (right image) and the “pleonaste sample” (middle), the shaped bodies containing ESS show a markedly improved alkali-resistance with the same initial weights of the components ESS (left image), pleonaste (middle), and hercynite (right image).

Finally, Fig. 10 shows the superiority of refractory products with ESS according to the invention, as compared to refractory products of the same composition with pleonaste. The left image in Fig. 10 shows a sample which was produced with 8.5% ESS. In each case the same grain size distributions of the main component, namely fused magnesia, and the spinel component were used. Additionally, the firing conditions were the same. After ceramic firing, the samples were subjected to a standardized thermal shock resistance test at 1200°C (30 cycles each of 30 minutes according to DIN EN 993-11).

The thermal shock resistance of the intact left sample containing ESS is clearly evident, while the right sample containing pleonaste is cracked.

Advantageous features of the invention will be listed below, wherein all features can be combined either individually or in various combinations with features of the main claim, independently of their order of listing in the respective subclaims.

The invention is characterized in particular by a granular elasticizer in the form of a crushed granulate for refractory products, in particular for basic refractory products, minerally consisting of mono-phased sintered spinel mixed crystals of the ternary system MgO-Fe_2O_3-Al_2O_3 of the composition range

MgO:	12 to 19.5, in particular 15 to 17 wt.-%,
Remainder:	Fe_2O_3 and Al_2O_3 in a quantity ratio range of Fe_2O_3 to Al_2O_3 between 80 to 20 and 40 to 60 wt.-%.

wherein, starting from an MgO content between 12 and 19.5 wt.-%, the respective mixed crystals have an Fe_2O_3 and Al_2O_3 content in a solid solution from the limited ranges indicated for each case, such that a total composition of 100 wt-% is obtained.

Furthermore it is an advantage if the elasticizer comprises:

a grain bulk density of ≥ 2.95, in particular ≥ 2.99, preferably ≥ 3.2 g/cm^3, quite particularly up to 3.7 g/cm^3, measured according to DIN EN 993-18

or

less than 5, in particular less than 2 wt-% of secondary phases

or

grain compressive strengths between 20 MPa and 35 MPa, in particular between 25 MPa and 30 MPa, measured with reference to DIN EN 13005 - Appendix C

or

linear coefficients of expansion α between 8.5 and 9.5, in particular between 8.8 and 9.2 • 10-6^{-1} K^{-1}

or

grain size distribution between 0 and 6, in particular between 0 and 4 mm, preferably with the following grain distributions, each with commonly standard grain

distributions, in particular Gaussian grain distributions, or with certain, selected grain fractions and/or grain bands.

0.5-1.0 mm 30-40 wt.-%

1.0-2.0 mm 50-60 wt.-%

The invention is characterized in particular also by a method for producing of a mono-phased sintered spinel, wherein

- at least one high purity, in particular powdered MgO component
- at least one high purity, in particular powdered Fe_2O_3-component
- at least one high purity, in particular powdered Al_2O_3-component

are mixed in a composition range according to claim 1 in amounts based on the oxides, and the mixture is sintered in a neutral or oxidizing atmosphere in a ceramic firing process until the respective monophasic sintered spinel mixed crystal formation is reached, and subsequently the sintered material is cooled, from which a sintered solid body or multiple sintered solid bodies result, which are then crushed into granulate, after which an elastifying granulate with predetermined grain composition is created, for example by sieving, out of the granulate.

It is also an advantage if the following method parameters are used:

- as MgO component at least one starting material from the following group is used: sintered magnesia, caustic magnesia, in particular with MgO contents greater than 96, preferably greater than 98 wt-%,
- as Fe_2O_3-component at least one starting material from the following group is used: magnetite or hematite, in particular with Fe_2O_3-contents greater than 90, preferably greater than 95 wt-%

- as Al_2O_3-component at least one starting material from the following group is used: alpha and/or gamma alumina, in particular with Al_2O_3 contents greater than 98, preferably greater than 99 wt-%, preferably alpha and gamma alumina.

Instead of the pure, premium primary raw materials normally used, also granulates from recycling materials can be used, such as mill scale (Fe_2O_3) or recycled magnesia stone (MgO) or magnesia-spinel stones (Al_2O_3, MgO), at least in partial quantities.

Furthermore it is an advantage if the components are crushed and mixed with grinding energy in a grinding machine, preferably up to a fineness ≤ 0.1, especially ≤ 0.05 mm.

or

the mixtures are sintered at temperatures between 1200 and 1700, in particular between 1400 and 1600 °C, preferably 1450 and 1550 °C, especially for 5 to 7 hours,

or

the mixtures are compacted before sintering, e.g. by granulation or compression, especially pressed into granules with volumes for example between 10 and 20, especially between 12 and 15 cm^3, as well as bulk densities for example between 2.90 and 3.20, especially between 3.0 and 3.1 g/cm^3 determined according to DIN EN 993-18, preferably with pressing forces between 40 MPa and 130 MPa, especially between 60 and 100 MPa. Pressed shaped bodies have volumes of, for example, between 1600 and 2000 cm^3.

The invention also pertains to a basic, ceramic fired or non-fired refractory product in the form of refractory shaped bodies, in particular compressed, shaped re-

fractory bodies, or in the form of non-shaped refractory masses comprising, in particular consisting of

50 to 95 wt-%, in particular 60 to 90 wt-% of at least one granular, basic, refractory material, in particular magnesia, in particular fused magnesia and/or sintered magnesia, with grain sizes e.g. between 1 and 7, in particular between 1 and 4 mm

0 to 20, in particular 2 to 18 wt-% of at least one powdered, basic, refractory material, in particular magnesia, in particular fused magnesia and/or sintered magnesia with grain sizes ≤ 1 mm, in particular ≤ 0.1 mm

5 to 20, in particular 6 to 15 wt-% of at least one granular elasticizing granulate according to the invention, with grain sizes e.g. between 0.5 and 4, in particular between 1 and 3 mm

0 to 5, in particular 1 to 5 wt-% of at least one powdered additive, e.g. from a powdered sintered spinel produced according to the invention with grain sizes ≤ 1 mm, in particular ≤ 0.1 mm

0 to 5, in particular 1 to 2 wt-% of at least one binder known for refractory products, in particular with at least one organic binder such as lignin sulfonate, dextrin, methyl cellulose, etc.

The refractory products according to the invention containing the elastifier granulates according to the invention are suitable in particular for use as the fire-side lining of industrial, large-volume furnace systems which are operating with a neutral and/or oxidizing furnace atmosphere, in particular for the lining of cement rotary kilns.

Claims

1. Granular, refractory mineral elasticizing granulate for refractory products, in particular for basic refractory products, minerally consisting of a monophased sintered spinel mixed crystal of the ternary system MgO-Fe_2O_3-Al_2O_3 of the composition range

MgO:	12 to 19.5, in particular 15 to 17 wt.-%,
Remainder:	Fe_2O_3 and Al_2O_3 in a quantity ratio range of Fe_2O_3 to Al_2O_3 between 80 to 20 and 40 to 60 wt.-%,

wherein starting from an MgO content between 12 and 19.5 wt.-%, the respective mixed crystals having an Fe_2O_3 and Al_2O_3 content in solid solution out of the limited ranges respectively indicated therefore, such that a total composition of 100% is obtained.

2. Elasticizing granulate according to claim 1,
characterized by
a bulk density of ≥ 2.95, in particular ≥ 2.99, preferably ≥ 3.2 g/cm^3, quite particularly up to 3.7 g/cm^3, measured according to DIN EN 993-18.

3. Elasticizing granulate according to claim 1 and/or 2,
characterized by
less than 5, in particular less than 2 wt-% of secondary phases.

4. Elasticizing granulate according to one or more of claims 1 to 3,
characterized by

grain compressive strengths between 20 MPa and 35 MPa, in particular between 25 MPa and 30 MPa, measured with reference to DIN EN 13005 (Appendix C).

5. Elasticizing granulate according to one or more of claims 1 to 4, **characterized by**
a linear coefficient of expansion between 8.5 and 9.5, in particular between 8.8 and 9.2 • 10^{-6} K^{-1}.

6. Elasticizing granulate according to one or more of claims 1 to 5, **characterized by** grain sizes with commonly standard grain distributions, in particular Gaussian grain distributions, or with certain grain fractions between 0 and 6, in particular between 0 and 4 mm, preferably with the following grain distributions:

0.5-1.0 mm 30-40 wt.-%

1.0-2.0 mm 50-60 wt.-%.

7. Method for producing of a mono-phased elasticizing granulate according to one or more of claims 1 to 6,
characterized in that

- at least one high purity, in particular powdered MgO component
- at least one high purity, in particular powdered Fe_2O_3-component
- at least one high purity, in particular powdered Al_2O_3-component

are mixed in a composition range according to claim 1 in amounts based on the oxides, and the mixture is sintered in a neutral or oxidizing atmosphere in a ceramic firing process until the respective monophasic sintered

spinel mixed crystal formation is reached, and subsequently the sintered material is cooled, from which a sintered solid body or multiple sintered solid bodies result, which are then crushed into granulate, after which an elastifying granulate with specific grain composition is created, for example by sieving, out oft he granulate.

8. Method according to claim 7,
characterized in that

- as MgO component at least one raw material from the following group is used: fused magnesia, sintered magnesia, caustic magnesia, in particular with MgO contents greater than 98, preferably greater than 98 wt-%, or an iron-rich, alpine sintered magnesia

- as Fe_2O_3 component at least one raw material from the following group is used: magnetite, hematite, mill scale, in particular with Fe_2O_3-contents greater than 90, preferably greater than 95 wt-%

- as Al_2O_3 component at least one raw material from the following group is used: aluminum oxide, in particular in the form of alpha or gamma alumina, in particular with Al_2O_3 contents greater than 98, preferably greater than 99 wt-%, or calcined metallurgical bauxite.

9. Method according to claim 7 and/or 8,
characterized in that
the components are mixed and/or crushed in a grinding machine, preferably up to a fineness of ≤ 0.5 mm, especially ≤ 0.1 mm.

10. Method according to one or more of claims 7 to 9,
characterized in that

the mixtures are sintered at temperatures between 1200 and 1700, in particular between 1400 and 1600 °C, preferably 1450 to 1550 °C, especially for 4 to 8 hours.

11. Method according to one or more of claims 7 to 10,
characterized in that
the mixtures are compacted before sintering, for example by granulating or pressing, especially pressing into granules with volumes for example between 10 and 20 cm^3, particularly between 12 and 15 cm^3, as well as bulk densities for example between 2.90 and 3.20, especially between 2.95 and 3.10 g/cm^3 determined according to DIN EN 993-18, preferably with pressing forces between 40 MPa and 130 MPa, especially between 60 and 100 MPa.

12. Basic, ceramic fired or non-fired refractory product in the form of shaped refractory bodies, in particular compressed shaped refractory bodies, or in the form of non-shaped refractory masses, comprising or in particular consisting of:

50 to 95 wt-%, in particular 60 to 90 wt-% of at least one granular, basic, refractory material, in particular magnesia, in particular fused magnesia and/or sintered magnesia, with grain sizes e.g. between 1 and 7, in particular between 1 and 4 mm

0 to 20 wt-%, in particular 2 to 18 wt-% of at least one powdered, basic, refractory material, in particular magnesia, in particular fused magnesia and/or sintered magnesia with grain sizes ≤ 1 mm, in particular ≤ 0.1 mm

5 to 20, in particular 6 to 15 wt-% of at least one granular elasticizing granulate according to the invention, with grain sizes e.g. between 0.5 and 4 mm, in particular between 1 and 3 mm

0 to 5 wt-%, in particular 1 to 5 wt-% of at least one powdered additive, e.g. from a sintered material produced according to the invention with grain sizes ≤ 1 mm, in particular ≤ 0.1 mm

0 to 5 wt-%, in particular 1 to 2 wt-% of at least one binder normally used for refractory products, in particular at least one organic binder such as dextrin, methyl cellulose, lignin sulfonate.

13. Use of an inventive refractory product according to claim 12, containing an elasticizing granulate according to one or more of claims 1 to 6, which is produced according to one or more of claims 7 to 11, as fire-side lining of large-volume, industrial furnace systems operated with a neutral or an oxidizing furnace atmosphere, in particular for the lining of cement rotary kilns.

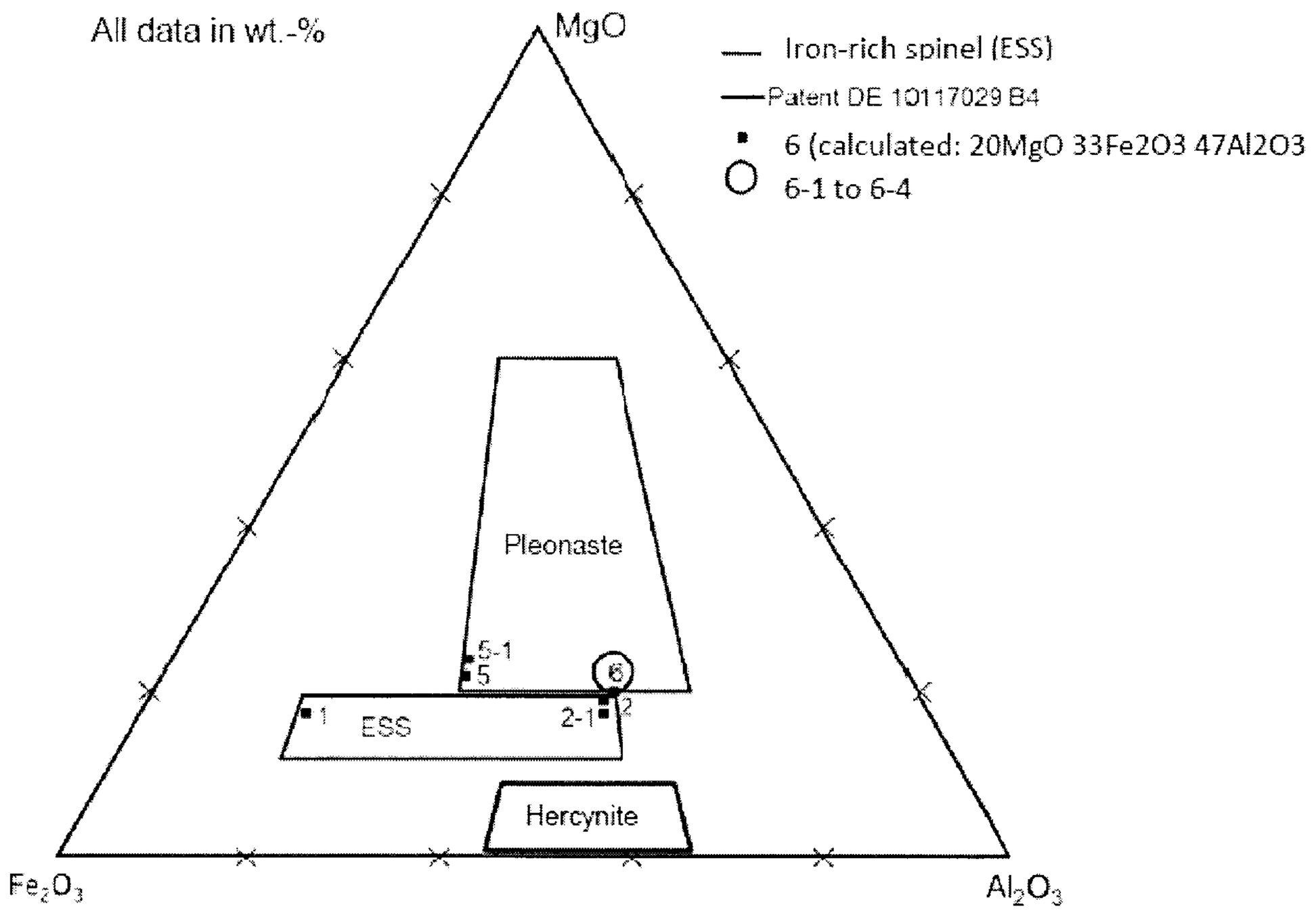

Fig. 1: System $MgO-Fe_2O_3-Al_2O_3$ (presented in wt.-%) with the claimed range of the present invention (ESS) as well as of the patent DE 10117029 B4 (pleonaste) and the range of the hercynite elastifier (DE 44 03 869 C2)

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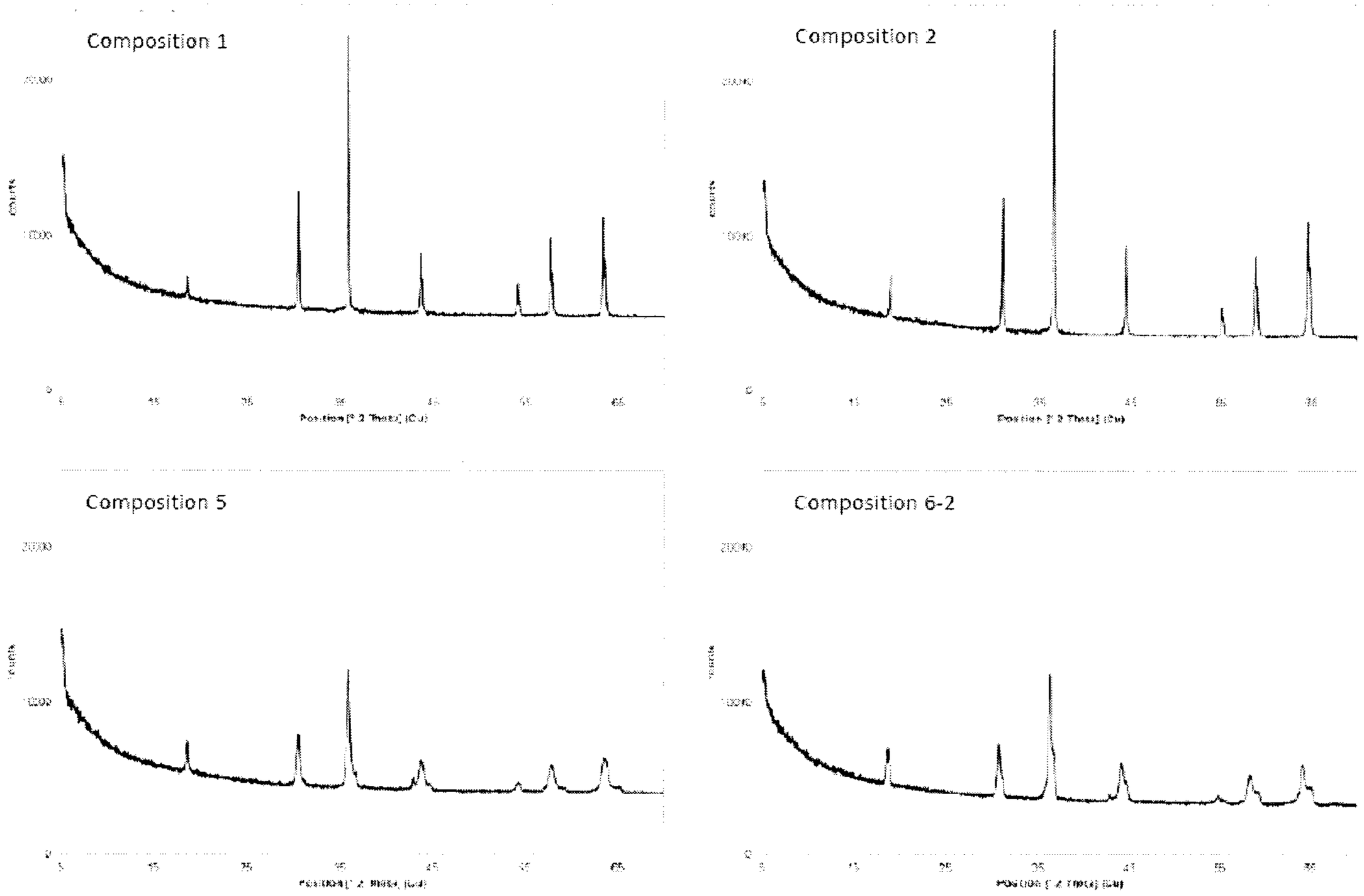

Fig. 2: X-ray powder diffractograms of the compositions synthesized in the system $MgO-Fe_2O_3-Al_2O_3$. The reflexes of compositions 1 and 2 have a low halfwidth. The positions and intensities of the reflexes can be explained by a single spinel phase. The reflexes of compositions 5 and 6-2 are less well-defined and have correspondingly high halfwidths. The positions and intensities of the reflexes can be explained by the coexistence of two spinel phases (spinel S1 ($MgFe_2O_4$ss) and spinel S2 ($MgAl_2O_4$ss))

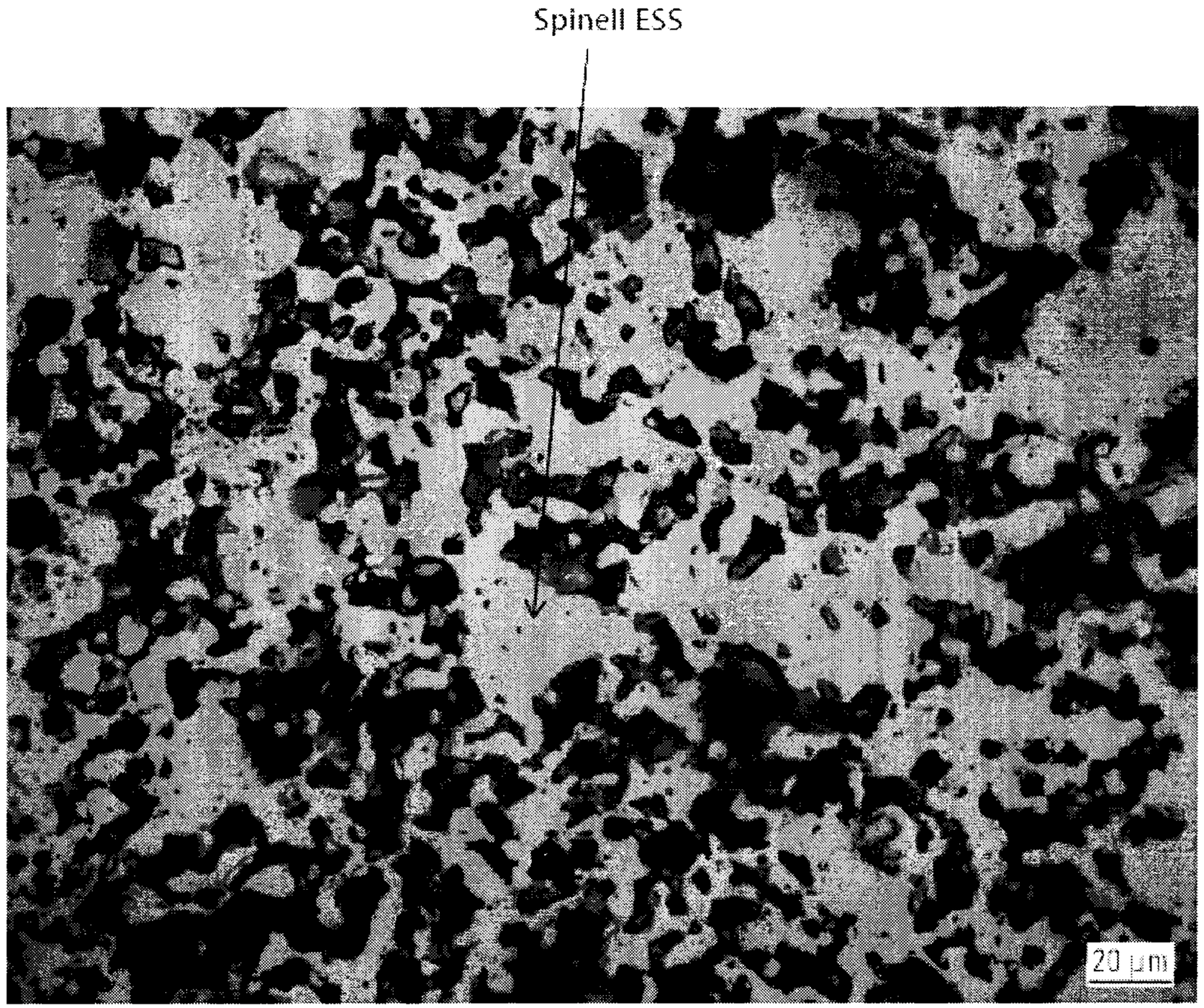

Fig. 3: Reflected-light microscopy – composition 1. A homogeneous reflection color of the synthesis product identifies the iron-rich sintered spinel of composition 1 as monophased. The dark areas are pores filled with epoxy resin.

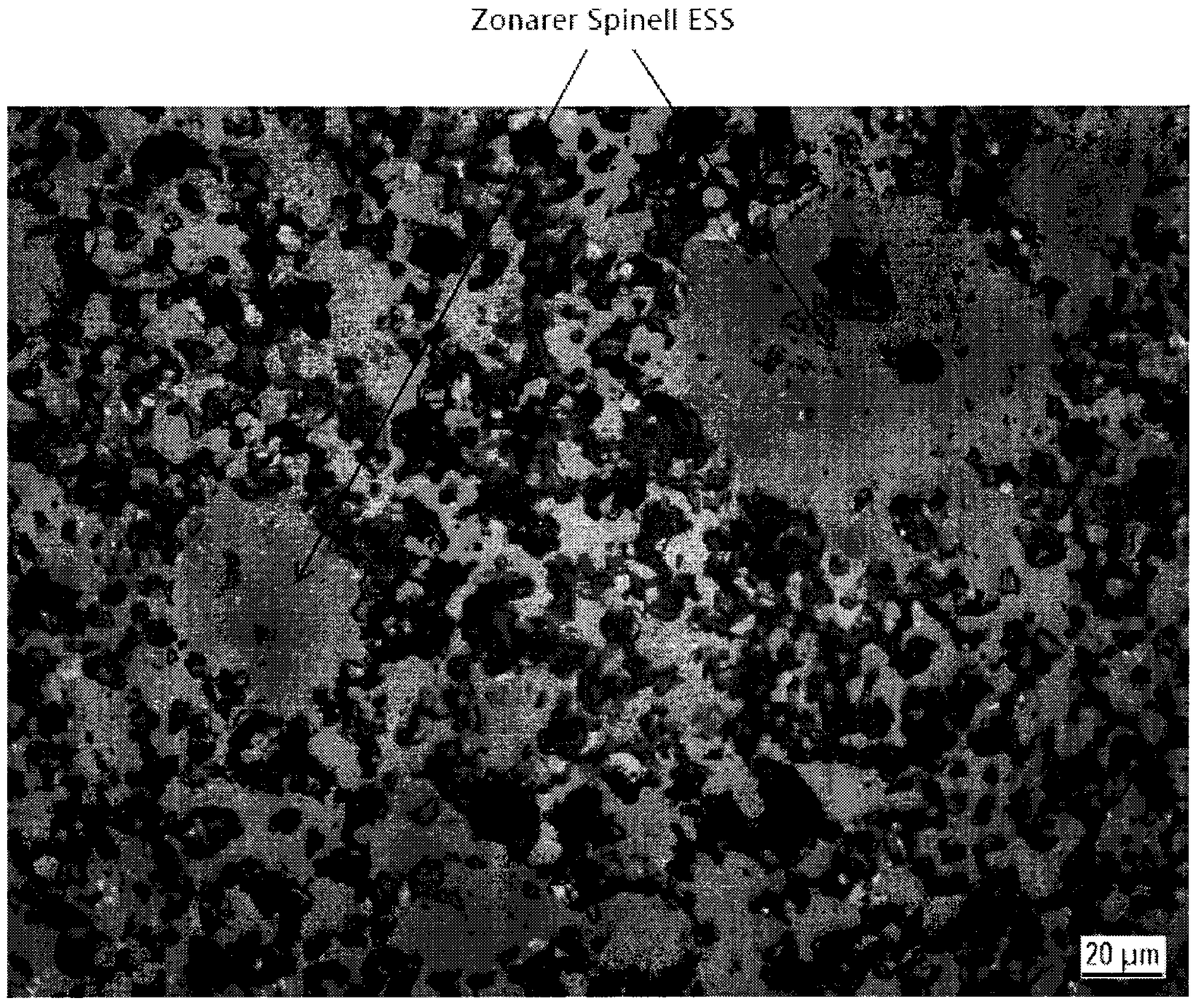

Fig. 4: Reflected-light microscopy – composition 2. A homogeneous reflection color of the synthesis product identifies the iron-rich sintered spinel of composition 2 as monophased, wherein the larger spinels comprise a zonar form due to incomplete equilibrium. The dark areas are pores filled with epoxy resin. The light areas are inner reflexes.

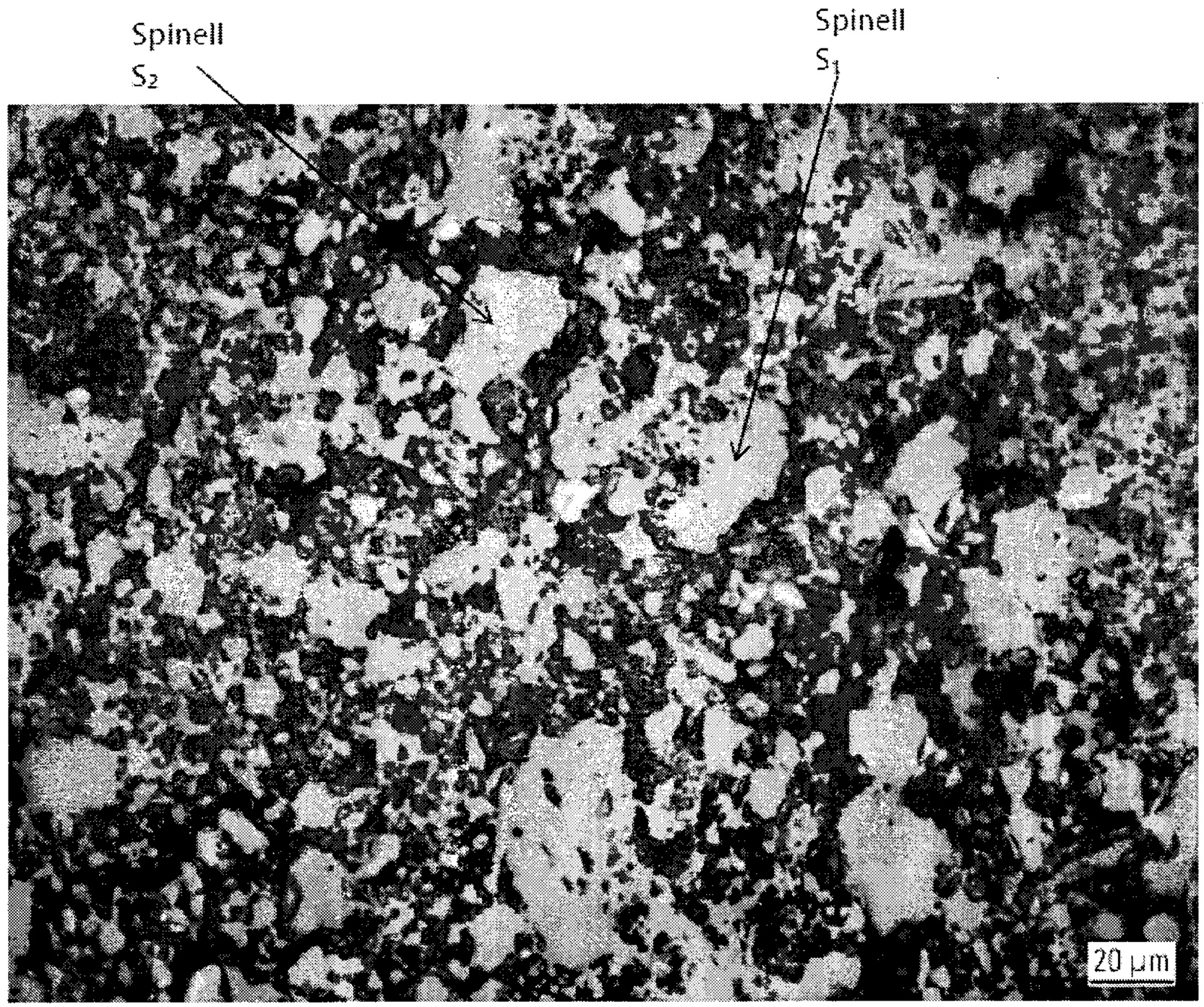

Figure 5: Reflected-light microscopy – composition 5. Two spinels can be distinguished based on the reflection colors and with reference to Kwestroo 1959: Spinel S1 ($MgFe_2O_4$ss) with gray-blue reflection color, and spinel S2 ($MgAl_2O_4$ss) with gray-pink reflection color. The dark areas are pores filled with epoxy resin.

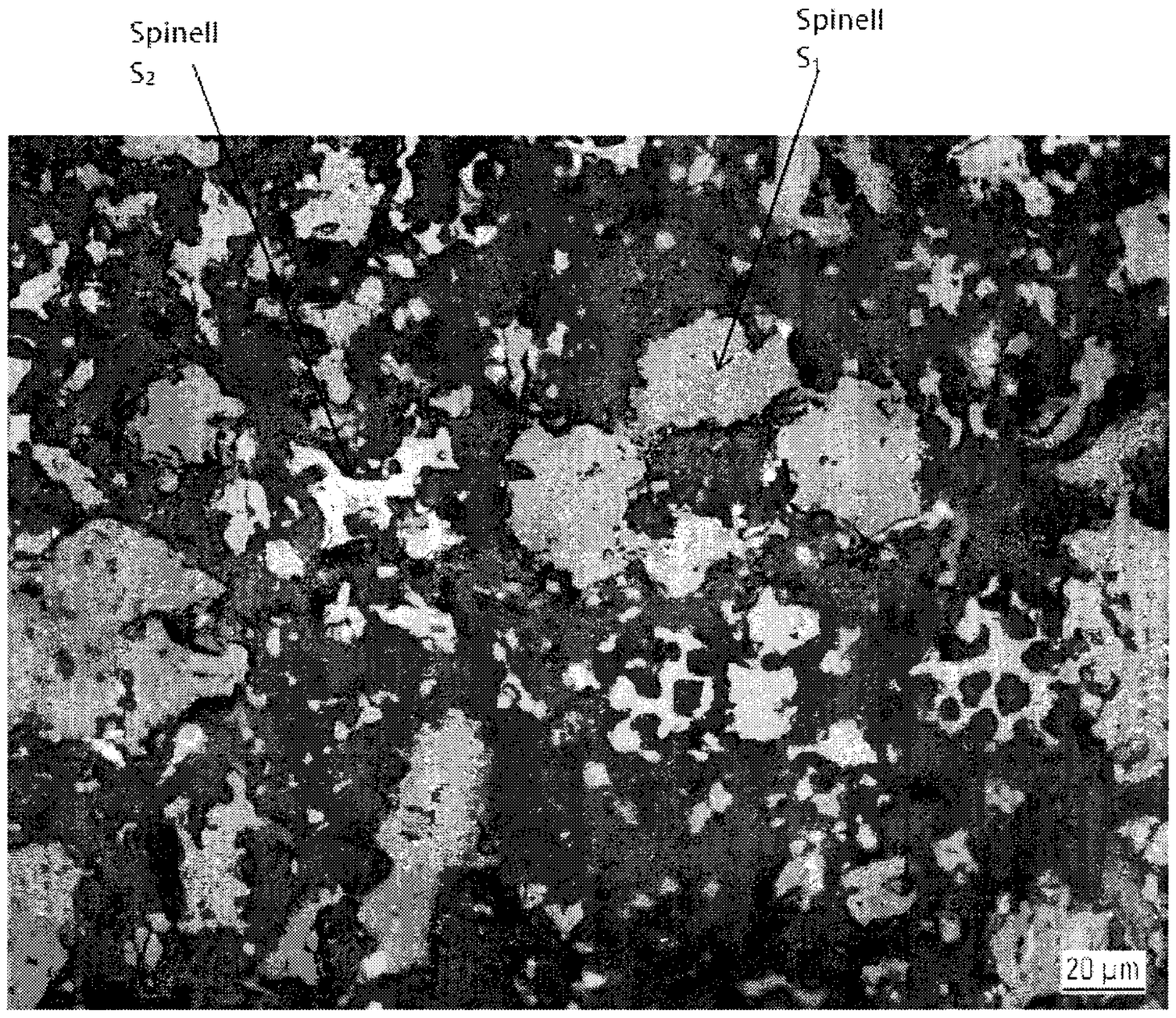

Fig. 6: Reflected-light microscopy – composition 6-2. Due to the reflection colors, using Kwestroo 1959 two spinels can be identified: spinel S1 ($MgFe_2O_4$ss) with gray-blue reflection color and spinel S2 ($MgAl_2O_4$ss) with gray reflection color. The dark areas are pores filled with epoxy resin.

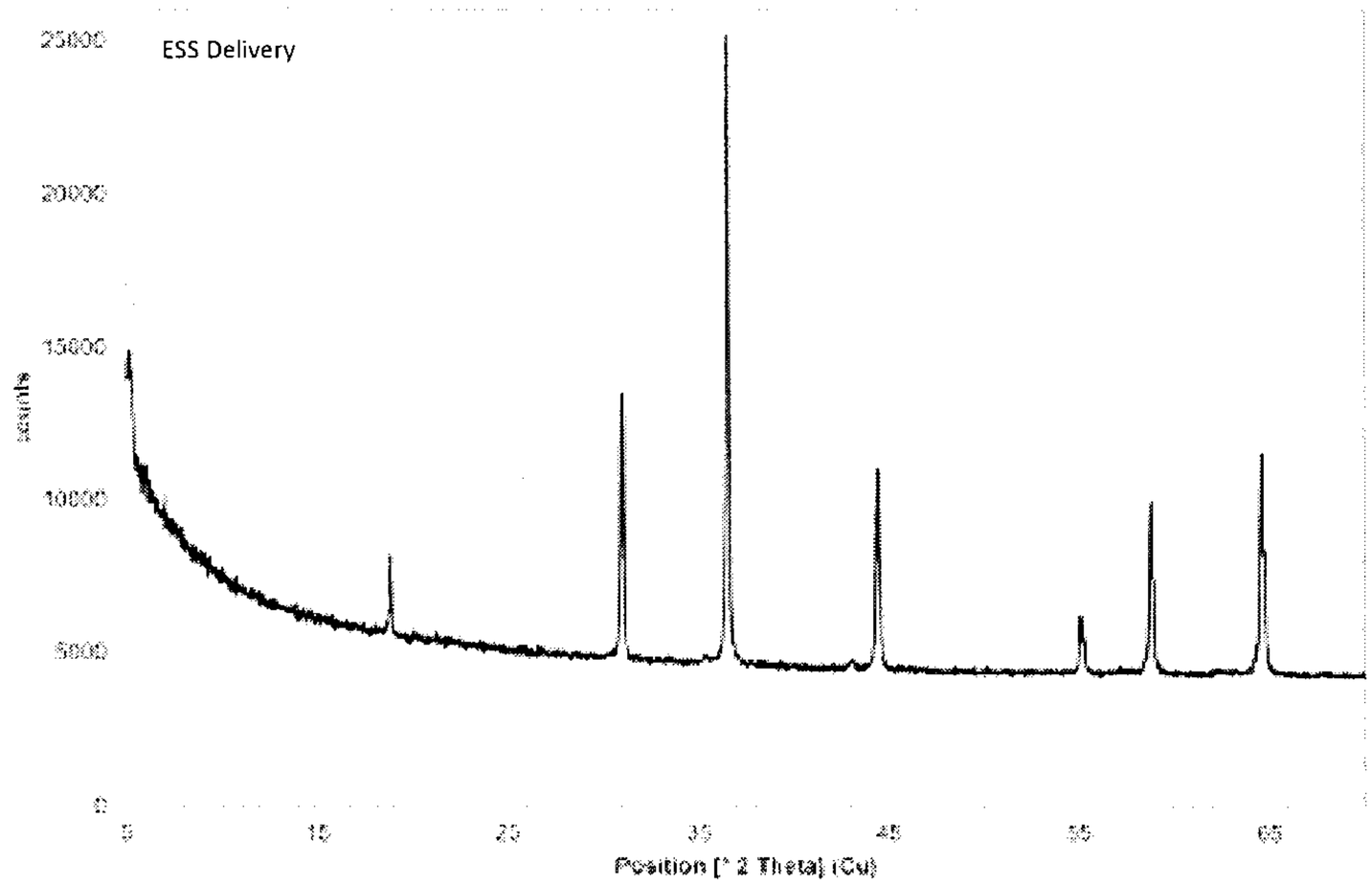

Fig. 7a: X-ray powder diffractogram of the iron-rich sintered spinel (ESS) as delivered

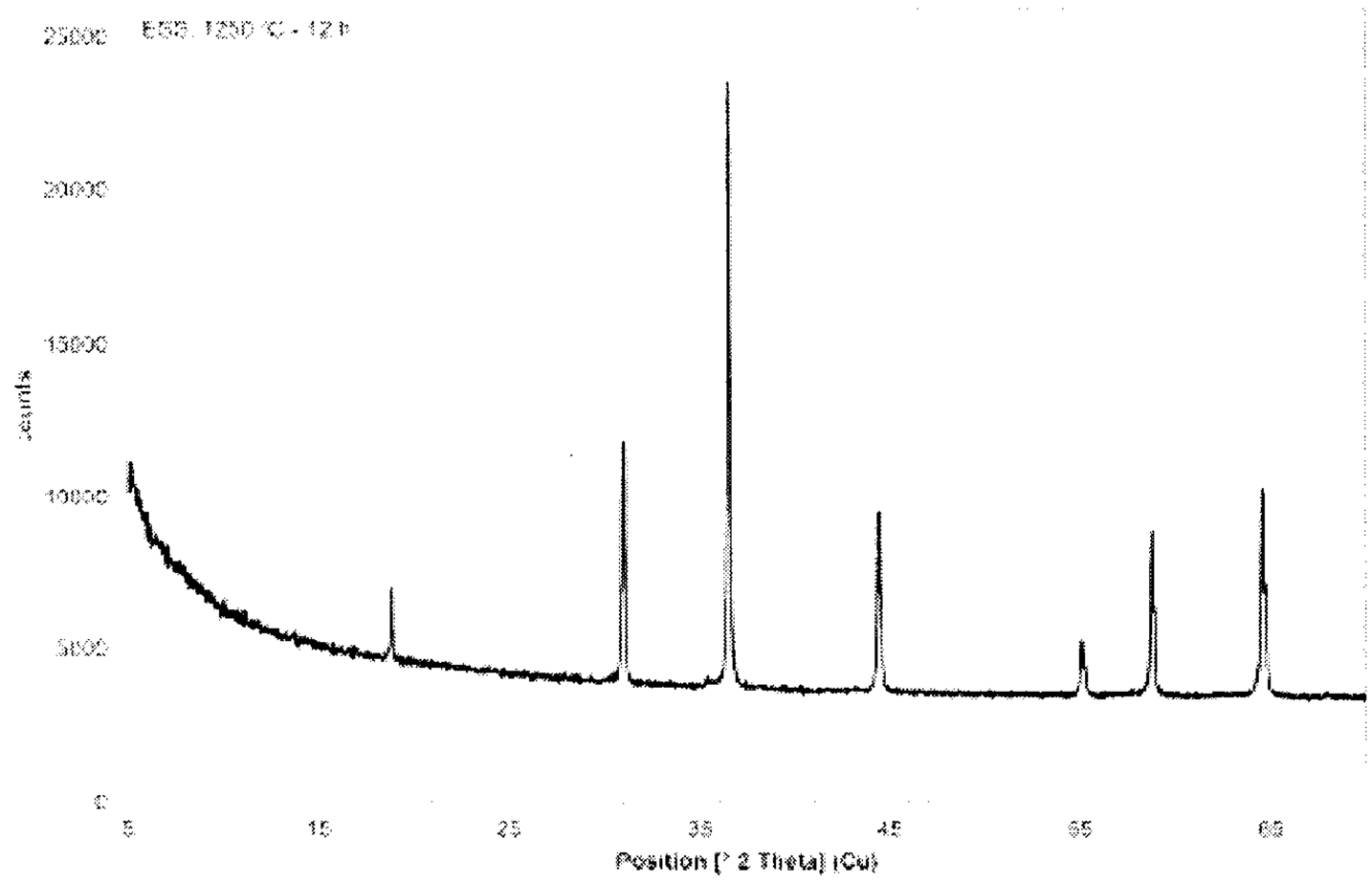

Fig. 7b: X-ray powder diffractogram of the iron-rich sintered spinel (ESS) after heat treatment under oxidizing conditions (1250°C / 12 h).

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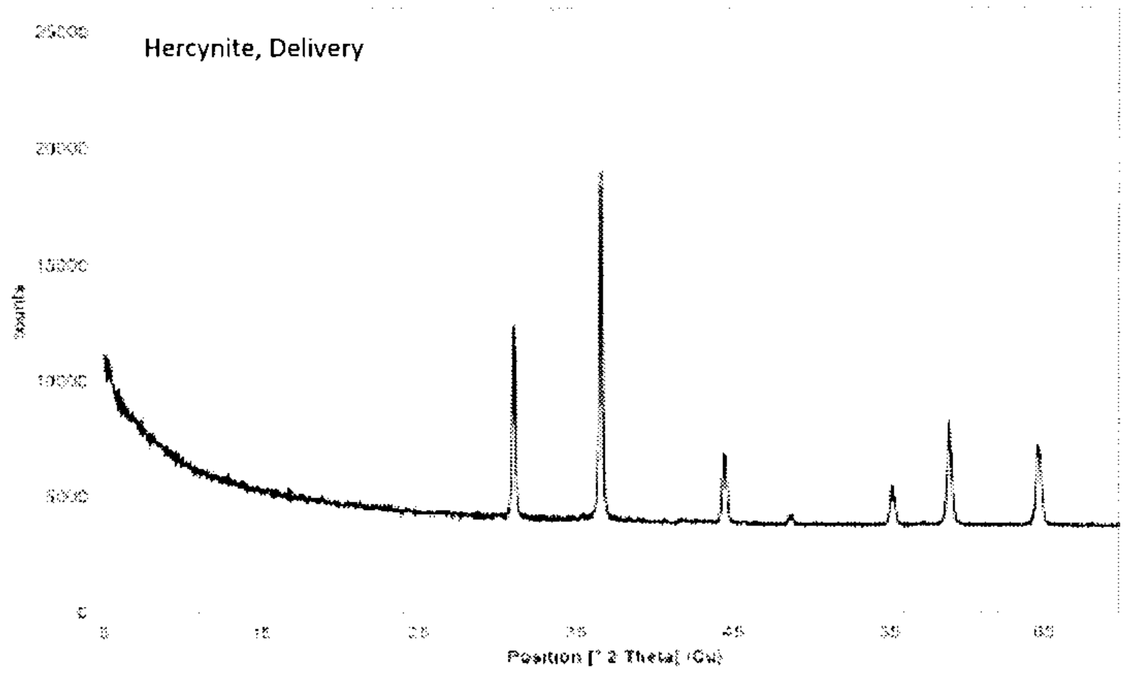


Fig. 8a: X-ray powder diffractogram of an industrially produced hercynite as delivered.

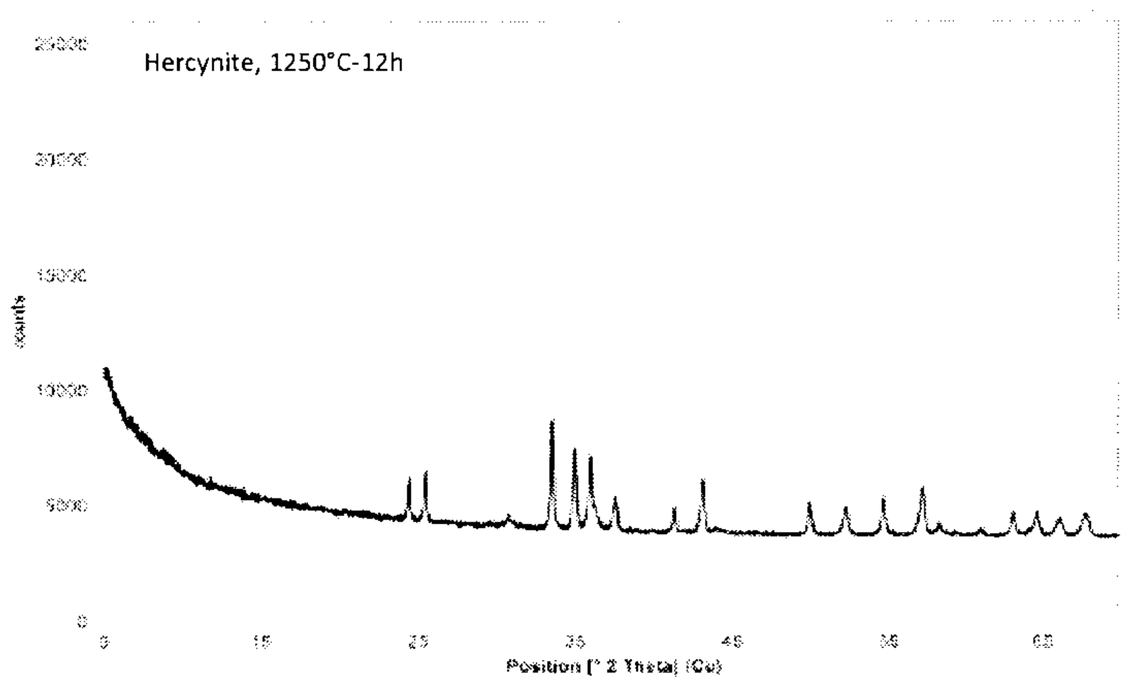


Fig. 8b: X-ray powder diffractogram of an industrially produced hercynite after heat treatment under oxidizing conditions (1250°C / 12 h). Due to extensive oxidation of the bivalent iron, the original spinel structure was destroyed.

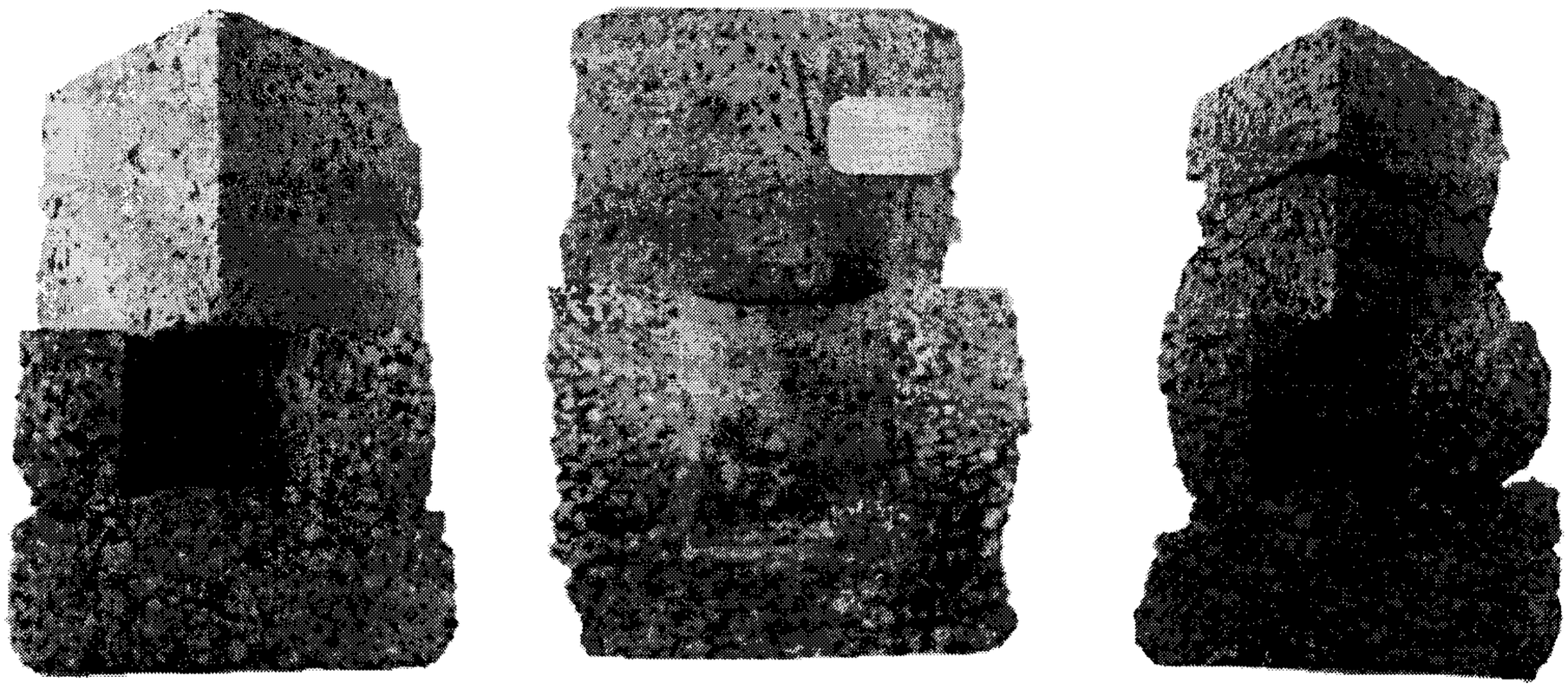


Fig. 9: The alkali resistance of basic magnesia shaped bodies containing iron-rich sintered spinel (ESS) were tested in a crucible at 1400°C (residence time 3h) with potassium carbonate as a reaction agent (left image). The test was conducted according to the "Test Methods for Dense Refractory Products - Guidelines for Examination of Fluid-Induced Corrosion of Refractory Products; German Edition, CEN/TS 15418, 2006". Compared to hercynite (right image) and fused pleonaste (middle, patent DE 10117029 B4), the shaped bodies containing ESS (left image) comprise markedly better alkali resistance with the same weights of components ESS (left image), fused pleonaste (middle) and fused hercynite (right image).

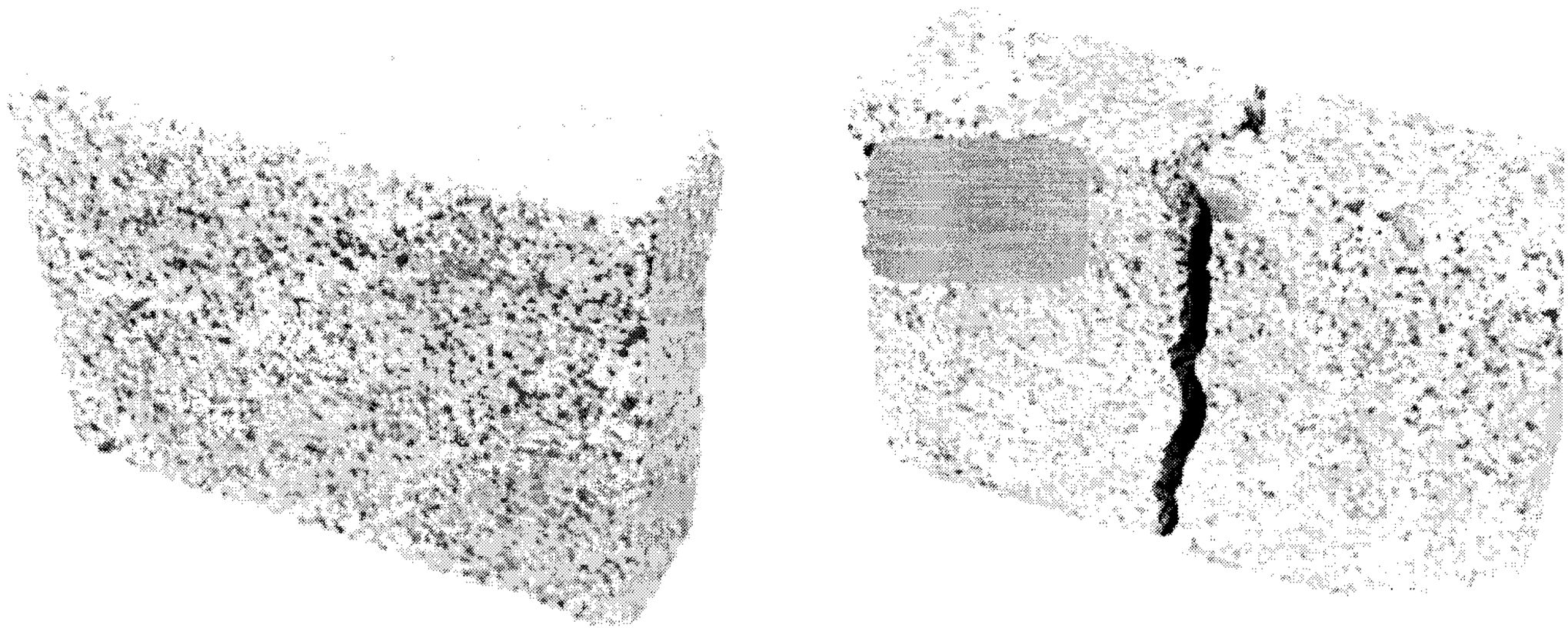
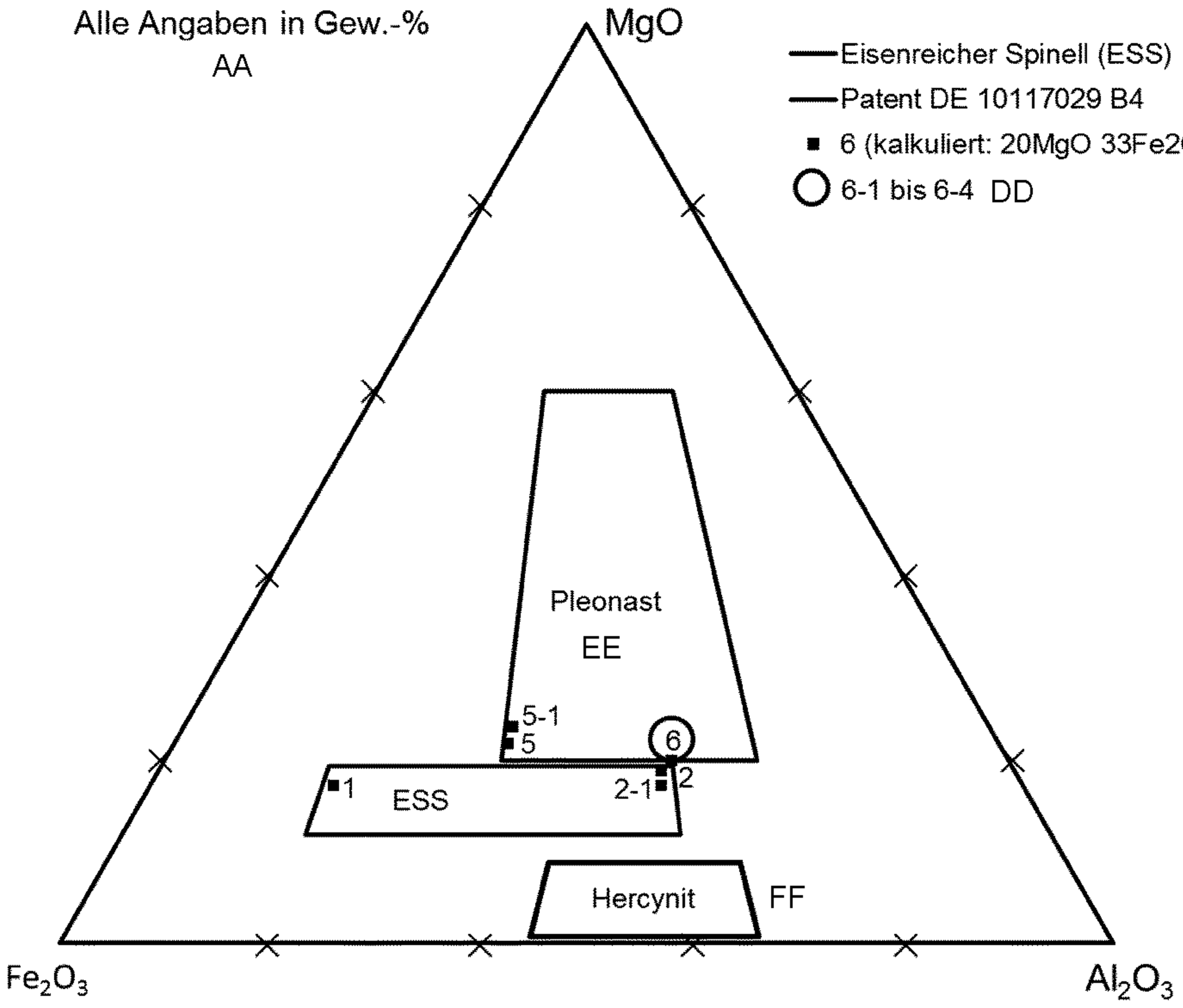


Fig. 10: Samples after temperature shock resistance test at 1200°C (30 cycles, each 30 minutes). Both refractory products have a comparable magnesia matrix (resistor). The left image shows a sample which was produced with 8.5% ESS, and the right image shows a sample produced with 8.5% fused pleonaste (comparable grain size distribution). The greater thermal shock resistance of the left sample is clearly evident.



GG

Fig. 1: System MgO-Fe_2O_3-Al_2O_3 (Darstellung in Gew.-%) mit dem beanspruchten Bereich der vorliegenden Erfindung (ESS) sowie des Patentes DE 10117029 B4 (Pleonast) und dem Bereich des Hercynit-Elastifizierers (DE 44 03 869 C2).

AA All indications in wt.-%
BB Iron-rich spinel (ESS)
CC 6 (calculated: 20MgO 33Fe2O3 47Al2O3)
DD 6-1 to 6-4
EE Pleonast
FF Hercynite
GG Fig. 1: System (MgO-Fe2O3-Al2O3 (shown in wt.-%) in the claimed range according to the invention (ESS) and according to patent DE 10117029 B4 (pleonast) and the range of the hercynite elasticizer (DE 44 03 869 C2).