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AUGITE CONTENT IN BASALT RAW MATERIAL AND THAT OF PYROXENE IN FUSED BASALT AND THEIR EFFECT ON THE MECHANICAL PROPERTIES OF THESE MATERIALS

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According to qualitative evaluation the pyroxene-augite amount in natural basalt is markedly lower than that of the newly formed pyroxene in fused basalt castings. These differences are explained and the qualitative finding has been proved quantitatively by X-ray determinations on the example of mass-produced fused olivine-basalt from the Nová Baňa locality.

INTRODUCTION

Basalts represent a large group of basic minerals. According to their composition they are divided into several subgroups. Extensive research has shown that only two subgroups of intermediate basalts, namely olivine-basalts and basanites [1] are suitable for petrurgical processing.

THEORETICAL CONSIDERATIONS ON THE CHANGE IN MINERALOGICAL COMPOSITION OF BASALT DUE TO FUSION AND NONEQUILIBRIUM CRYSTALLIZATION

The natural basalts which comply with the petrurgical specifications contain the basic crystalline phases within the following limits [1]:

augite	45 to 60 % by vol.
feldspars—plagioclases	15 to 30 % by vol.
foids (nepheline)	0 to 10 % by vol.
olivine	10 to 20 % by vol.
magnetite	5 to 10 % by vol.

Crystallization of melts of these natural basalts [2] yields materials containing mostly pyroxene (similar to augite) the amout of which as compared with the original raw material is substantially increased at the expense of all the other phases. There are also minor amounts of olivine which usually grows on the imperfectly fused particles of natural basalt, and magnetite may likewise be present. No feldspars and foids arise during the crystallization of industrially manufactured fused basalt products.

There is a question of the function of the oxidic feldspar component and of the partially unprecipitated olivine and magnetite during the crystallization of the basalt melt. Logically one may derive that for the most part these components will participate in the formation of pyroxene (the proportion of which has been substantially raised by fusion and recrystallization) and a smaller proportion will remain in the residual glassy phase which does not occur nearly at all in natural basalts but constitutes about 10% or more of fused crystallized basalt.

The final representation of phases in the crystallized product may be estimated on the basis of microscopic examination of planar distribution as follows:

pyroxene	70 to 90 % by vol.
olivine	0 to 10 % by vol.
magnetite	3 to 7 % by vol.
residual glass	5 to 15 % by vol.

However, this crystalline product does not differ only in the phase composition of the precipitated crystalline phases but also in a quite different texture: Whereas natural basalts are characterized by larger phenocrysts in particular of olivine or augite (sometimes even of feldspar) embedded in a fine-grained matrix (Fig. 1), a fused crystallized product typically comprises fine-grained skeletal or spheroidal pyroxene crystals surrounded by the residual glassy phase and thus has a texture quite different from that of the original natural basalt (Figs. 2 and 3). These differences are due to a number of factors (such as that of pressure, 'dry'melt, mineralizers, etc.) but in particular to the fact that in nature the magma had crystallized exceedingly slowly (usually for several years) so that there was time enough for the formation of fully shaped idiomorphous crystals (phenocrysts) and a virtually equilibrium state has been established at virtually all temperatures. On the other hand, a fused basalt casting solidifies within several minutes (3 to 5) so that the crystallization proceeds without any partial equilibrium states and the phases precipitating at the highest temperatures (magnetite and olivine) barely manage to crystallize; in the crystallization of pyroxene a significant role is played by the ability of wider isomorphous substitution of ions in the crystalline lattice.

The present study had the aim of verifying quantitatively this qualitative and mostly theoretical assumption of the increased pyroxene content in fused basalt of the Nová Baňa type. (Figs 1, 2, 3 in Appendix.)

VERIFICATION OF THE PRELIMINARY CONCLUSIONS

Evaluation of the Nová Baňa natural basalt

According to petrographic analysis of the Nová Baňa basalt the augite content in the entire igneous formation varies to a quite considerable degree in its individual magmatic streams.

Fiala [3] reports on data determined on the basis of precise planimetric measurements of polished sections. The following augite contents were found at the individual places: 60.7, 52.4, 57.4, 62.9, 59.2 %, that is in the range of 52 to 63 %. Kopecký [2] estimates an approximate mean augite content of 50 % in basalt from the old quarry.

Quantitative X-ray determination of augite and pyroxene

Since optical analysis had not been found suitable for quantitative determination of pyroxene content in fused basalt tiles owing to the fine-grained dendritic, skeletal or spheroidal pyroxene crystals, use was made of the internal standard X-ray analysis [4]. Its principle is based on the fact that the relation of integral intensity of the X-ray diffraction line of a given crystalline phase and of the diffraction line of the standard substance is a linear function of the concentration of the crystalline phase being determined if the amount of the standard substance is kept constant. Considerable experience has already been gained with the application of the method in the field of silicates. Let us just mention two cases from the field of glass-ceramics which are close to the petrurgical problems.

Kitaigorodskii et al. [5] determined quantitatively the quartz, rutile and spinel phases in glass ceramics in the system SiO_2—Al_2O_3—MgO using the internal standard method (CaF_2) and direct measurement of internal reflection intensity. The standard curves were determined by means of rock quartz crystal and natural rutile. The spinel was synthetized. Both methods have yielded satisfactory accuracy and agreement of the results.

Tokareva et al. [6] combined in a suitable way the internal standard method (TiO_2) with that of X-ray diffraction of the amorphous phase ($2\Theta = 22.5$ deg.) on variously heat treated cordierite and spodumen based materials. The β-spodumen and cordierite standards were obtained by crystallization of the respective glasses. The results of determinations of the two crystalline phases and of the residual glassy phase were in a comparatively good agreement.

As has already been mentioned the author had the aim of simultaneously comparing the augite content in the basalt raw material extracted in the new Nová Baňa quarry with that of pyroxene crystallized in a casting made of this raw material. It was therefore necessary to carry out quantitative determination of both phases; however, this task was quite difficult as the composition of natural augites in the individual types of basalts is subject to considerable variations and the composition of pyroxene precipitating during crystallization of the basalt melt is unknown and would obviously also vary to a substantial degree with the individual basalt types. However, since the structure of pyroxenes both crystallized in nature and prepared artificially is basically identical in spite of marked differences in chemical composition, their X-ray diffractograms are also quite similar. For the sake of simplicity, diopside, as the basic mineral of the pyroxenes group, has been chosen as standard.

Preparation of diopside

As the composition of natural diopsides also shows marked variations, use was made of synthetic diopside $CaMgSi_2O_6$ fused from chemically pure substances in a PtRh crucible at 1500 °C for 5 hours. The melt had been stirred continuously during the melting. The homogeneous melt was then poured into water and the resulting frit ground into a fine powder which was completely crystallized by heat treatment at 1000 °C for 3 hours. X-ray and microscopy analyses have proved the crystalline substance to comprise pure diopside virtually free from glassy phase.

Preparation of samples and measurement

Standard mixtures of crystallized diopside and of the original diopside glass (frit) with a constant addition of the NaCl internal standard were then prepared in the usual way. Samples for X-ray analysis were prepared from very finely powdered (grain size 400 mesh) and thoroughly homogenized mixtures by compacting. The GON-03 instrument (made by Chirana N.C.) with a GM counter was used in the measurements under the following conditions: Cu X-ray tube radiation (30 kV, 16 mA), Ni filter, diffractometer inlet slot width 5′, slot width in front of GM counter 2′, counter movement speed 1°/min.

The diffractograms obtained were evaluated according to the peak heights of the respective lines as well as according to their area. The $d = 2.98$ Å and $d = 2.821$ Å lines were chosen for evaluation for diopside and NaCl respectively. More accurate results were obtained by evaluating the peak heights of the individual lines and a calibration diagram was constructed (Fig. 4) for evaluating the content of augite and pyroxene in the respective samples. The accuracy of measurement on standard mixtures was about 5 %.

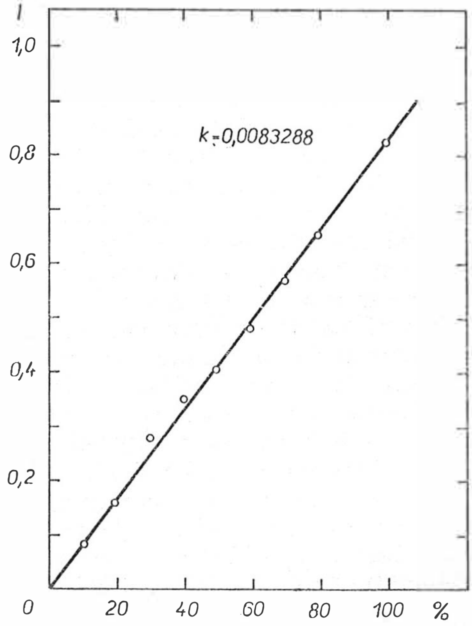

Fig. 4. Standard diagram for quantitative X-ray diffraction determination of pyroxene and augite.
Synthetic diopside sample.

RESULTS

The following contents of the dominant crystalline phase in basalt were determined by the internal standard method:
in natural raw material from the new quarry 54.2 ± 7.5 % augite,
in primarily crystallized tile 80.6 ± 8.1 % pyroxene.

The agreement with petrographic evaluation of the natural raw material which had been carried out by Fiala is very satisfactory since all the values reported by this author were in the range of 54.2 ± 7.5 %, so that any possible objection that a somewhat different type of diopside was employed for calibration need not be regarded as significant. The considerable dispersion of results in both determinations is quite understandable since the composition variations of the originally relatively coarse-grained mineral already follows from the results by Fiala [3] and in the case of the casting itself there arises a crystallization gradient which must necessarily have an effect on pyroxene and residual glassy phase content.

DISCUSSION

The determinations have confirmed fully the preceding theoretical conclusions in that nonequilibrium primary crystallization of basalt melts yields substantially higher proportions of pyroxene and also allowed to explain why fusion and subsequent crystallization bring about an improvement of the basic mechanical properties of the initial raw material (Table I).

Table I

The basic mechanical properties of the natural rock and of a Nová Baňa fused basalt casting

Property	Natural basalt	Tile
Compression strength	310 MPa	540 MPa
Abrasion grinding hardness	790 cm²/cm³	1600 cm²/cm³

The basalt tile showed compression strength and abrasion hardness values virtually twice as high as those of natural basalt [7]. The compression strength established is in a quite satisfactory agreement with the mean strength of basalt usually specified as up to 300 MPa. This relatively low value is related above all to the size and type of the crystals present. Apart from the quite fine-grained matrix natural basalt contains certain proportions of larger crystals, the so-called phenocrysts, which in the Nová Baňa basalt attain sizes of up to 2—3 mm. Smaller augite phenocrysts are also sometimes found. It can be readily comprehended that at the contact area of a phenocryst with the matrix or rather at that of phenocrysts of two different minerals the different thermal expansions of the two crystals may result in considerable stresses which in many cases would create fine cracks. During the mechanical tests these points exhibit the lowest strength and become the starting points of failure.

In the abrasion hardness tests the stressing by the abrasive grains results in easy breaking out of phenocrysts from the matrix and thus in considerable losses of the abraded material; moreover, these crystals themselves take part in the abrasion process.

On the other hand, basalt castings exhibit substantially finer crystallization. The individual spherolitic, skeletal or dendritic crystals are firmly embedded in the ambient glassy phase so that any stress that could cause cracking is far less likely to arise. For this reason mechanical tests result in failure only at much higher loading. The individual fine crystals are much more resistant to breaking out of the matrix in the abrasion hardness tests.

There may be many more causes of the differences in strength and hardness; mention was made only of the most significant ones related to crystal size.

CONCLUSION

X-ray quantitative determinations have shown that rapid nonequilibrium crystallization of fused basalt under operational conditions results in the crystallization of substantially higher proportions of pyroxene than can be found in natural basalt. It has been explained on the basis of different sizes of crystals of the main minerals why the recrystallized basalt materials show markedly superior mechanical properties.

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OBSAH AUGITU V ČEDIČOVÉ SUROVINĚ A PYROXENU V TAVENÉM ČEDIČI A JEHO VLIV NA MECHANICKÉ VLASTNOSTI TĚCHTO MATERIÁLŮ

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Pro rovnovážnou krystalizaci pomalu tuhnoucího čedičového magmatu v přírodě je charakteristické vylučování řady minerálů a hrubozrnná textura. Nerovnovážná krystalizace rychle ochlazované čedičové taveniny se naopak vyznačuje menším počtem vylučovaných fází, jiným jejich procentuálním zastoupením, přítomností zbytkové skelné fáze a podstatně jemnozrnnější texturou.

U petrurgicky vhodných basanitů a olivínických čedičů lze podíl jednotlivých fází v přírodní surovině a v přetavené rekrystalované hmotě zhruba odhadnout (viz tab.).

Ve výrobcích z taveného čediče silně převládá pyroxen na úkor plagioklasu a nefelinu (které se po přetavení nevylučují) a částečně olivínu a magnetitu (které se vylučují v nižším obsahu).

Porovnání obsahu augitu v přírodní hornině s pyroxenem v odlitcích z taveného čediče bylo provedeno u provozně taveného čediče Nová Baňa pomocí kvantitativního rentgenografického stanovení metodou vnitřního standardu (NaCl). Ke stanovení kalibračních křivek bylo použito synteticky připraveného diopsidu. Obsah augitu v přírodním čediči Nová Baňa činil 54,2 ± 7,5 %. Obsah novotvořeného pyroxenu v čedičové dlaždici činil 80,6 ± 8,1 %.

Fáze	Přírodní čedič % obj.	Přetavená rekrystalovaná hmota % obj.
augit—pyroxen	45—60	70—90
plagioklas	15—30	—
nefelin	0—10	—
olivín	10—20	0—10
magnetit	5—10	3—7
zbytkové sklo	—	5—15

Na základě zvýšeného podílu pyroxenu v odlitcích a jejich jemnozrnnější textury bylo v diskusi zdůvodněno prakticky dvojnásobné zvýšení mechanických vlastností (pevnost v tlaku a brusná tvrdost) ve srovnání s přírodní horninou.

Obr. 1. Olivínický čedič Nová Baňa — přírodní hornina s většími vyrostlicemi olivínu a augitu (1 až 2 mm).
Obr. 2. Sférolitický vývoj novotvořeného pyroxenu v taveném čediči Nová Baňa, který zkrystaloval při teplotách pod 1000 °C.
Obr. 3. Kostrovitý vývoj novotvořeného pyroxenu v odlitku z taveného čediče Nová Baňa, který zkrystaloval při teplotách nad 1100 °C. Hmota obsahuje nedotavené krystalky původního olivínu.
Obr. 4. Cejchovní graf ke kvantitativnímu rentgenografickému stanovení pyroxenu a augitu. Vzorek syntetický diopsid.

СОДЕРЖАНИЕ АВГИТА В БАЗАЛЬТОВОМ СЫРЬЕ И ПИРОКСЕНА В РАСПЛАВЛЕННОМ БАЗАЛЬТЕ И ЕГО ВЛИЯНИЕ НА МЕХАНИЧЕСКИЕ СВОЙСТВА ПРИВЕДЕННЫХ МАТЕРИАЛОВ

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Для равновесной кристаллизации медленно застывающего базальтового магмата в природе типично выделение ряда минералов и крупнозернистая текстура, в то время как неравновесная кристаллизация быстро охлаждаемого базальтового расплава отличается меньшим количеством выделяемых фаз, другим их процентным составом, присутствием остаточной стекловидной фазы и существенно более мелкозернистой структурой.

У петрургически пригодных базанитов и оливинических базальтов предполагаются в природном сырье и в расплавленной рекристаллизированной массе следующие доли отдельных фаз (таблица).

В изделиях из расплавленного базальта сильно преобладает пироксен за счет плагиоклаза и нефелина (которые после переплава не выделяются) и частично оливина и магнетита (которые выделяются в значительно меньшем количестве).

Сопоставление содержания авгита в природной горной породе с пироксеном в отливках из расплавленного базальта проводили в производственно расплавленном базальте Нова Баня с помощью количественного рентгеноагрфического определения методом внутреннего стандарта (NaCl). Для определения кривых калибрации использовали синтетически полученный диопсид. Содержание авгита в природном базальте Нова Баня составляло 54,2 ± 7,5 %. Содержание вновь образовавшегося пироксена в базальтовой плитке составляло 80,6 ± 8,1 %.

Фаза	Природный базальт % по объему	Расплавленная рекристаллизованная масса % по объему
Авгит-пироксен	45—60	70—90
Плагиоклаз	15—30	—
Нефелин	0—10	—
Оливин	10—20	0—10
Магнетит	5—10	3—7
Остаточное стекло	—	5—15

На основании повышения доли пироксена в отливках и их мелкозернистой текстуры рассматривается и обосновывается двухкратное повышение механических свойств (прочность при сжатии и абразивная твердость) по сравнению с природной горной породой.

Рис. 1. Оливинический базальт Нова Баня — природная порода с большими вкраплениями оливина и авгита (1—2 мм).

Рис. 2. Сферолитическое развитие вновь образовавшегося пироксена в расплавленном базальте Нова Баня, кристаллизующего при температурах ниже 1000 °С.

Рис. 3. Скелетовидное развитие вновь образовавшегося пироксена в отливке из расплавленного базальта Нова Баня, кристаллизующего при температурах выше 1100 °С. В массе содержатся кристаллики первоначального оливина, не подвергшиеся полному расплаву.

Рис. 4. График калибрации для количественного рентгенографического определения пироксена и авгита. Проба из синтетического диопсида.

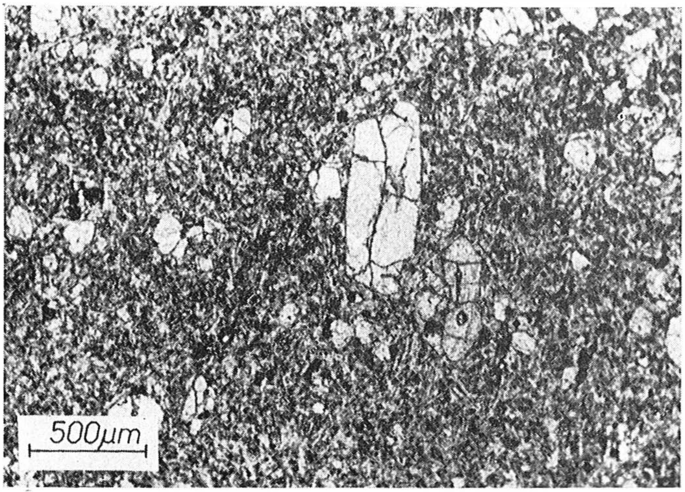

Fig. 1. Olivinitic basalt Nová Baňa — natural rock with coarser phenocrysts of olivine and augite (1 to 2 mm).

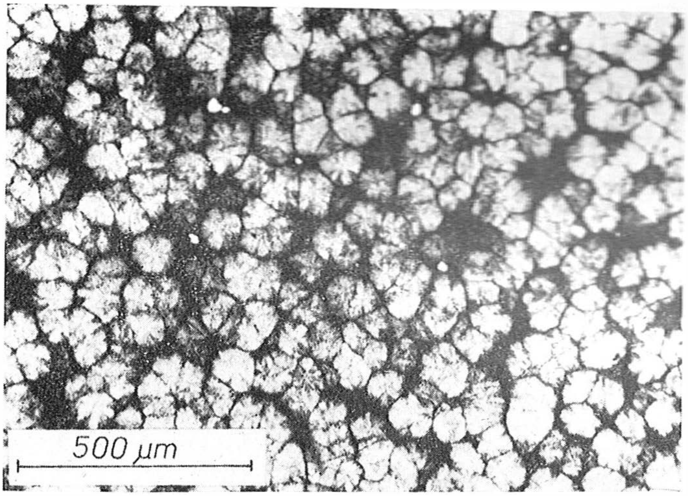

Fig. 2. Spherolitic development of newly formed pyroxene in the Nová Baňa fused basalt which has crystallized at temperatures below 1000 °C.

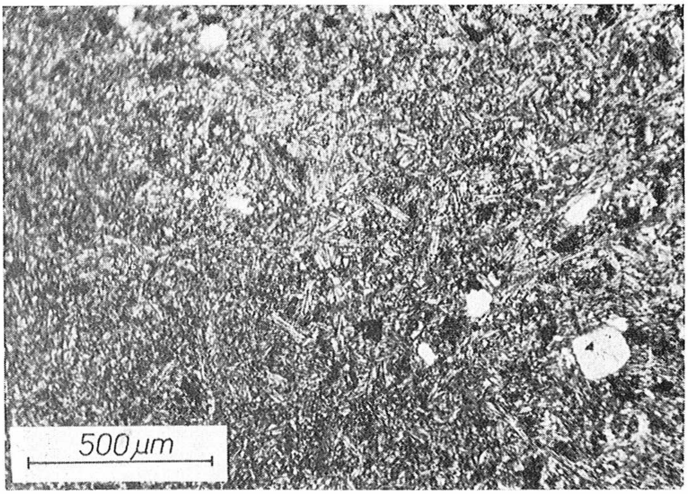

Fig. 3. Skeletal development of newly formed pyroxene in a Nová Baňa basalt casting which has crystallized at temperatures above 1100 °C. The material contains unfused crystals of original olivine.