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Dedicated to Professor Ionel Haiduc,
President of The Romanian Academy at his 70th anniversary

CRYSTALLIZED GLASSES WITH ADDITION OF FLY ASH

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ABSTRACT. Waste recycling represents a very significant issue for the protection of our environment. Large waste quantities (slag and ashes) are products of the coal extraction industry and its subsequent combustion in thermal power stations. The aim of this paper is to study the possibility of using fly ash from thermal power stations as a raw material in the process of obtaining crystallized glasses. Several glass samples, containing variable fly ash quantities, were elaborated and studied comparatively. The ash was used as a replacement for some initial raw materials. Optical and electronic microscopy, X-ray diffraction and thermo-differential analysis were used for the comparative study.

Introduction

One of the biggest problems for the environmental protection is the recycling of secondary and waste products. These are very well known as generators of impact and risk for the environment and public health. Among the most know are slag heaps, tars and ashes from thermal power stations. All of these are coal burning wastes and usually come in great quantities composing a large part of the environmental pollution problem.

Fly ashes from thermal power stations can be added to the process of obtaining binders, since they are silica-aluminous materials with slow hardening properties. Moreover, they are used as filling materials and to obtain some lightweight aggregates. Their usage for the production of concretes is restricted by the coal content, which should be bellow 3%, due to the fact that it reduces concretes resistance [1].

About 20-30% of the fly ash is used, the remaining quantity is deposited and thus constituting a chemical pollution source, but also an unused economic value.

Vitrification is one of the most efficient methods to reduce the wastes volume by transforming them into potential resources. Recent

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studies [2,3,4] indicate the possibility of capitalizing fly ashes by using them as raw materials to obtain crystallized glasses.

The aim of this paper is to study the possibility of using fly ashes from the Rovinari thermal power station as raw materials to obtain crystallized glasses.

Experimental procedure

In order to choose an oxidic system to obtain these glasses, the fly ashes were firstly characterised.

The mean oxidic composition of the ash (Table 1) indicate a large quantity of silica (54.62%) and iron oxide (7.9%), but also a large quantity of coal (33.03%) which are usually lost as volatile components during further combustion.

Table 1.
The mean oxidic composition of Rovinari fly ash (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	LOI
Fly ash	54.62	1.6	7.9	0.1	1.7	0.85	0.2	33.03

The thermal analysis of the fly ash was performed with a MOM derivatograph up to 1000°C at a heating rate of 10°C/min. The reference sample was Al_2O_3 and the samples were placed in ceramic crucibles.

The oxidation process of coal residues, during combustion, can be observed as an exothermic effect on the DTA curve, between 400-600℃ (see Figure 1).

Subjected to a thermal treatment at 1300℃, with on e hour plateau, the ash was transformed in an insufficiently melted material, with numerous voids due to the elimination of volatile components. The ash used in following experiments was initially calcinated in an air laboratory furnance in order to eliminate the carbon residues.

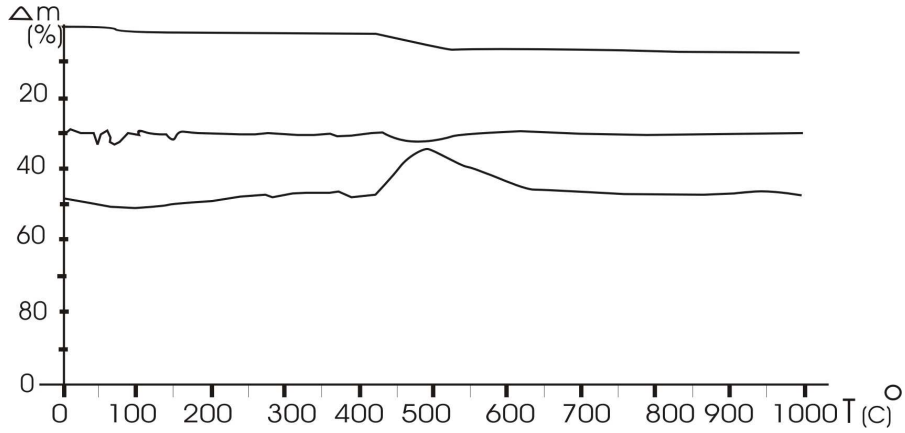


Figure 1. Differential Thermal Analysis curves of the Rovinari fly ash

The choice concerning the oxidic system for the desired crystallized glasses was taken considering the oxidic composition of the ash (high iron oxide content) and also the burning temperature of the samples, as a practical reason. Thus, the basic SiO_2-CaO-F_2O_3 oxidic system was chosen.

Using literature data [5], the composition of a reference sample was established as: SiO_2 = 44.69%; Fe_2O_3 = 24.35%; CaO = 21.25; Al_2O_3 = 6.27%; MgO = 3.14%. Quartz powder, KO1 kaolin, $FeSO_4*7H_2O$, $CaCO_3$ and $MgCl_2*6H_2O$ were used as raw materials [see Table 2].

Table 2.
The oxidic composition of the raw materials (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	TiO_2	LOI
Ash	54.62	1.6	7.9	0.1	1.7	0.85	0.2	-	33.03
Calcina-ted Ash	81.56	2.39	11.8	0.15	2.54	1.27	0.3	-	-
KO1 kaolin	43.55	38.58	0.8	0.2	0.2	0.3	0.19	0.19	14.79
Quartz powder	99.27	0.1	0.06	0.06	0.02	0.12	0.0	-	0.3
$FeSO_4*7H_2O$	-	-	28.72	-	-	-	-	-	71.27
$CaCO_3$	-	-	-	-	-	56	-	-	44
$MgCl_2*6H_2O$	-	-	-	-	-	-	19.8	-	80.17

Partial replacement of $FeSO_4*7H_2O$ with ash was sought. From the total quantity of 23.45% Fe_2O_3, different ratios of 5%, 10%, 15% and 20%, respectively, came from fly ashes. Nucleation agents, i.e. TiO_2 and Cr_2O_3, were used for samples R1 and R7. The former constituted the reference sample and the latter contained the larges amount of fly ash. Both nucleation agents were added in excess of 4%. The recipes of the studied glasses are given in Table 3.

The melting treatment was achieved in a laboratory electrical furnace at a maximum temperature of 1300℃, with on e hour plateau. Next, the melts where leaked out on a plane surface.

The reference sample R1 was subjected to thermal analysis in order to establish the crystallization thermal treatment. The thermal analysis of the glass was performed in the same way as for the fly ash. An exothermic effect was observed in the temperature range 800-900℃ (see Figure 2).

The crystallization thermal treatment was carried out in two ways:

1. - the samples, obtained after a quick cooling of the melts, were heated up to 850℃ and were kept at this temperatur e for periods between 1 and 5 hours for each sample;

2. - after the initial thermal treatment, the obtained melts were slowly cooled down to 850℃ and kept at this tempe rature for 10 hours.

Table 3.
Recipes of the studied glasses (wt%)

	Ash	Calci-nated Ash	SiO_2	KO1 kaolin	$FeSO_4$* $7H_2O$	$MgCl_2$* $6H_2O$	$CaCO_3$	Nucle-ators	
R1	-	-	19.74	8.4	43.84	8.09	19.93	TiO_2	Cr_2O_3
R_1N_1			19.74					4	
R_1N_2									4
R2	39.9	-	-	6.9	33.56	3.24	19.36		
R3	-	35.33	-	6.6	32.09	7.45	18.53		
R4	-	5.43	15.69	8.2	42.41	8.13	20.1		
R5	-	11.1	11.55	7.97	40.91	8.19	20.31		
R6	-	16.84	7.28	7.79	39.29	8.27	20.53		
R7	-	22.89	2.82	7.58	37.58	8.35	20.76		
R_7N_1	-	22.89	2.82	7.58	37.58	8.35	20.76	4	
R_7N_2	-	22.89	2.82	7.58	37.58	8.35	20.76		4

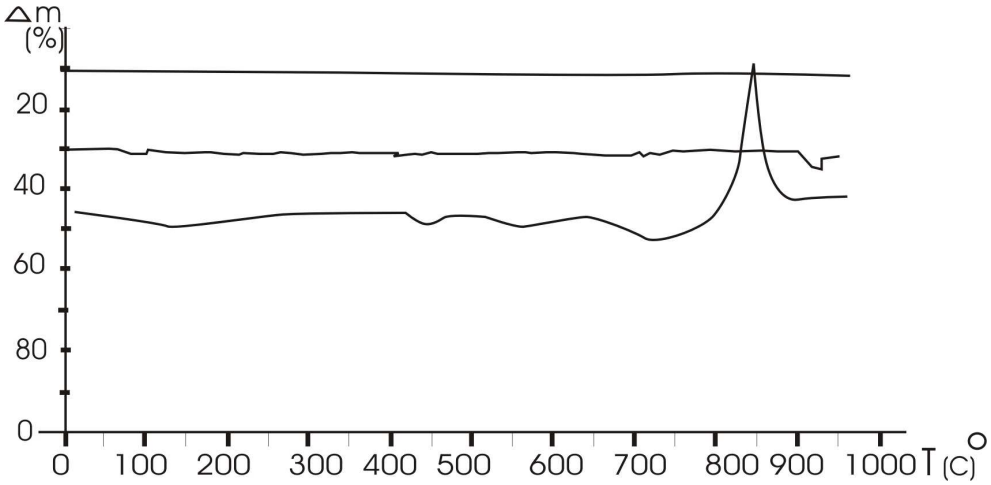


Figure 2. Differential Thermal Analysis curves for the R1 sample

The obtained glasses were studied through:
- Optical microscopy using an optical microscope with polarized light;
- Scanning electron microscopy using a JEOL-100S microscope;
- X-ray diffraction using a DRON3 diffractometer with CuKα radiation.

Results and discussions

Figure 3 contains optical microscopy images for the samples which underwent the first crystallization thermal treatment.

Figures 4 and 5 contain results of the same investigation method for the second thermal treatment samples.

Analysing the microscopy data, the following can be stated:

- the samples which were thermally treated for short periods presented an isotropy similar to glasses, with imperceptible crystallization phenomena;
- the R1 reference sample, treated at 850℃ through heating, did not present a perceptible crystalline structure, not even after a 5 hour thermal treatment (see Figure 3 – a, b, c);
- for the samples R7 with high ash content, small and unevenly distributed crystals were observed (see Figure 3 – f, g, h);
- the difference between the samples R1 and R7 shows the nucleation function of the fly ash, which might be explained by the different way of introducing Fe_2O_3 (as $FeSO_4$ or as Fe_2O_3 from the ash);
- the slowed cooling treatment applied to melts favoured the appearance of phase separations and crystals even for the sample which did not contain any ash.

Generally, there are two types of crystals in the samples. A third one can also be observed in the contact area between the melt and the crucible (see Figure 4a). The samples containing nucleators presented a higher tendency to crystallize. TiO_2 favoured the growth of black dentritical crystals dispersed in a glassy matrix of a lighter colour in both R1N1 (see Figure 4c) and R7N1 (see Figure 5b).

Macroscopically, the samples containing Cr_2O_3 present a surface with voids which can be explained to a possible reaction between itself and a mixture component that leads to gaseous products. The pores can be observed in the microscopic section (see Figure 4d and Figure 5c). The crystals which are developed in the vitreous matrix, in the presence of Cr_2O_3, are different from the TiO_2 ones and presented anisotropy.

The difference between the two nucleators was highlighted through SEM (see Figure 6). Figures 6a and 6b present the samples R1 and R7 and figures 6c and 6d present the samples R7N1 and R7N2 without nucleators which underwent the second crystallisation thermal treatment.

Also, the vitreous phase separation, which is more pronounced in sample R7N2, can be observed through SEM (see Figure 6d).

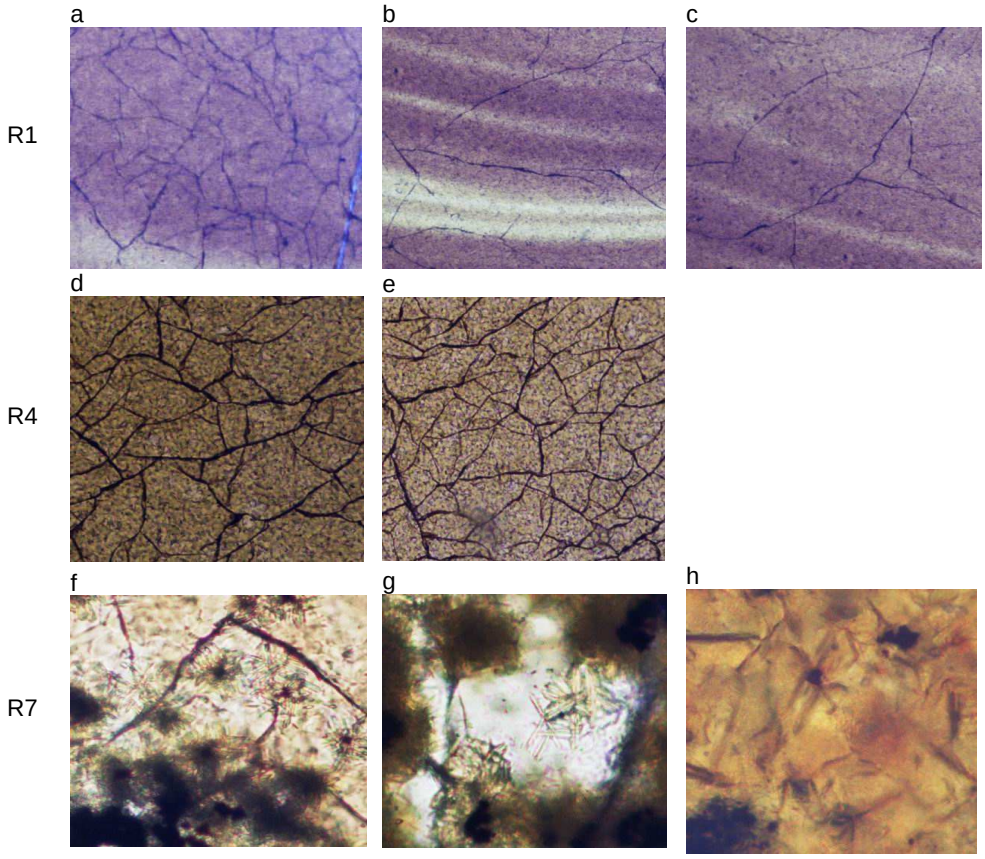


Figure 3. Optical microscopy images of the samples obtained after the first crystallization thermal treatment (x90)

R1 – a – R1 sample thermal treated at 850^{o}C – 1h plateau
b – R1 sample thermal treated at 850^{o}C – 3h plateau
c – R1 sample thermal treated at 850^{o}C – 5h plateau
R4 – d – R4 sample thermal treated at 850^{o}C – 1h plateau
e – R4 sample thermal treated at 850^{o}C – 3h plateau
R7 – f – R7 sample thermal treated at 850^{o}C – 1h plateau
g – R7 sample thermal treated at 850^{o}C – 3h plateau
h – R7 sample thermal treated at 850^{o}C – 5h plateau

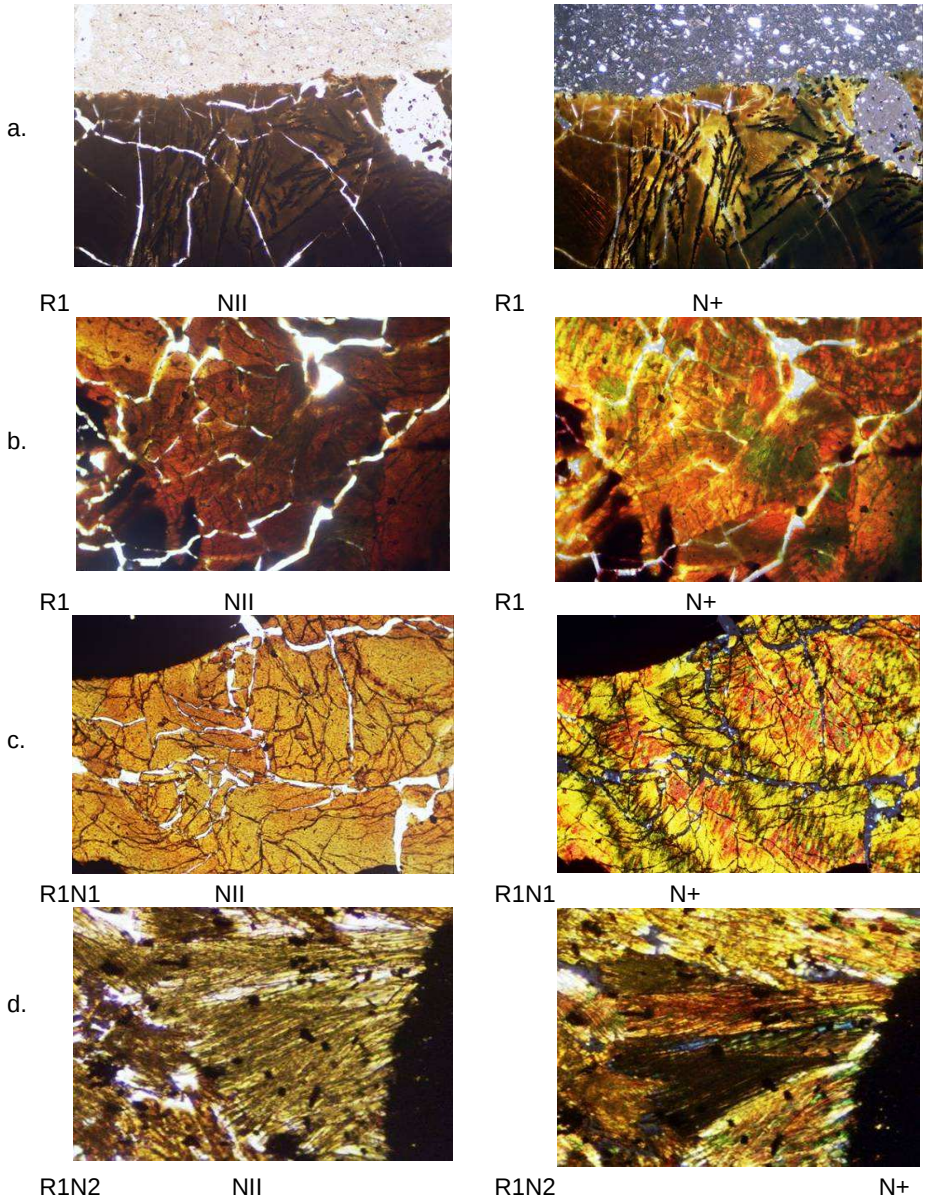


Figure 4. Optical microscopy images of the R1 sample obtained after the second crystallization thermal treatment (x90)

a, b – the R1 sample thermal treated at 850^{o}C – 10h plateau
c – the R1 sample with TiO_2 nucleator thermal treated at 850^{o}C – 10h plateau
d – the R1 sample with Cr_2O_3 nucleator thermal treated at 850^{o}C – 10h plateau
NII – parallel nicols; N+ - crossed nicols

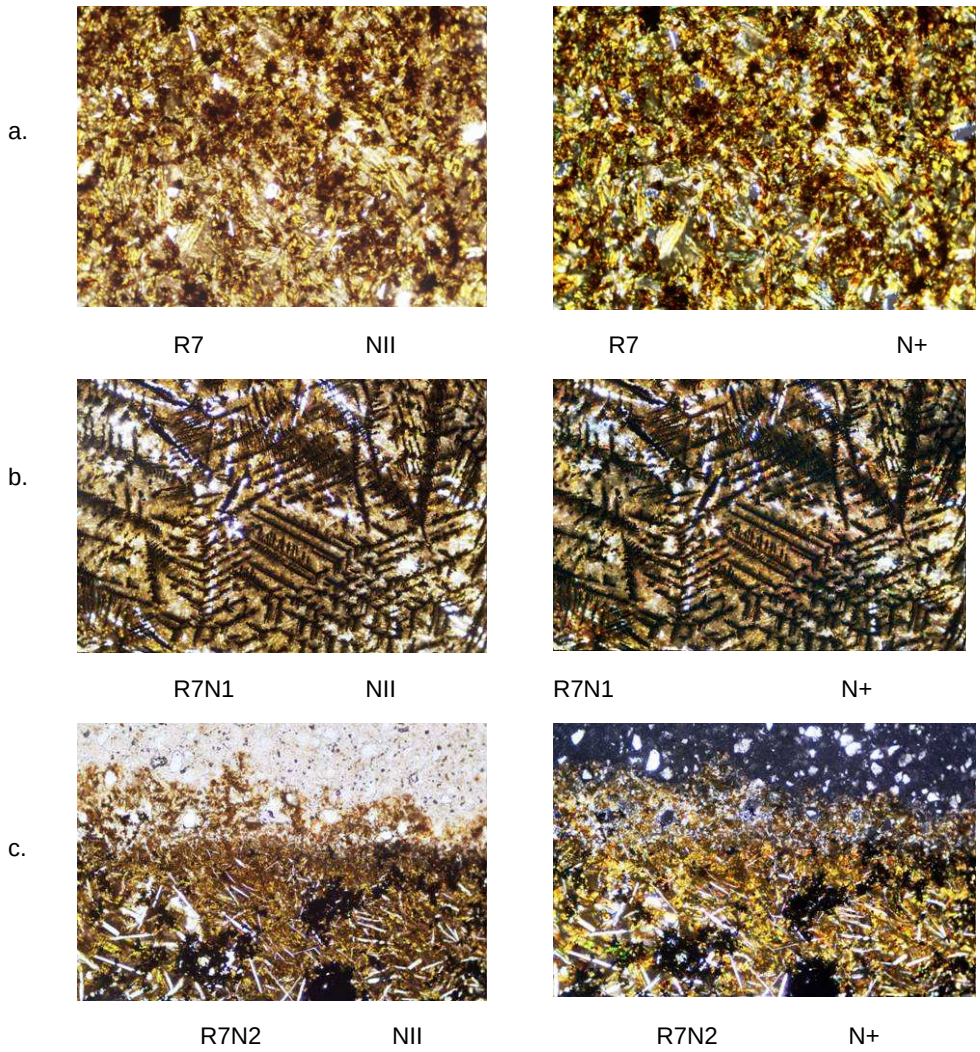


Figure 5. Optical microscopy images of the R7 sample obtained after the second crystallization thermal treatment (x90)

a – the R7 sample thermal treated at 850^{o}C – 10h plateau
b – the R7 sample with TiO_2 nucleator thermal treated at 850^{o}C – 10h plateau
c – the R7 sample with Cr_2O_3 nucleator thermal treated at 850^{o}C – 10h plateau
NII – parallel nicols; N+ - crossed nicols

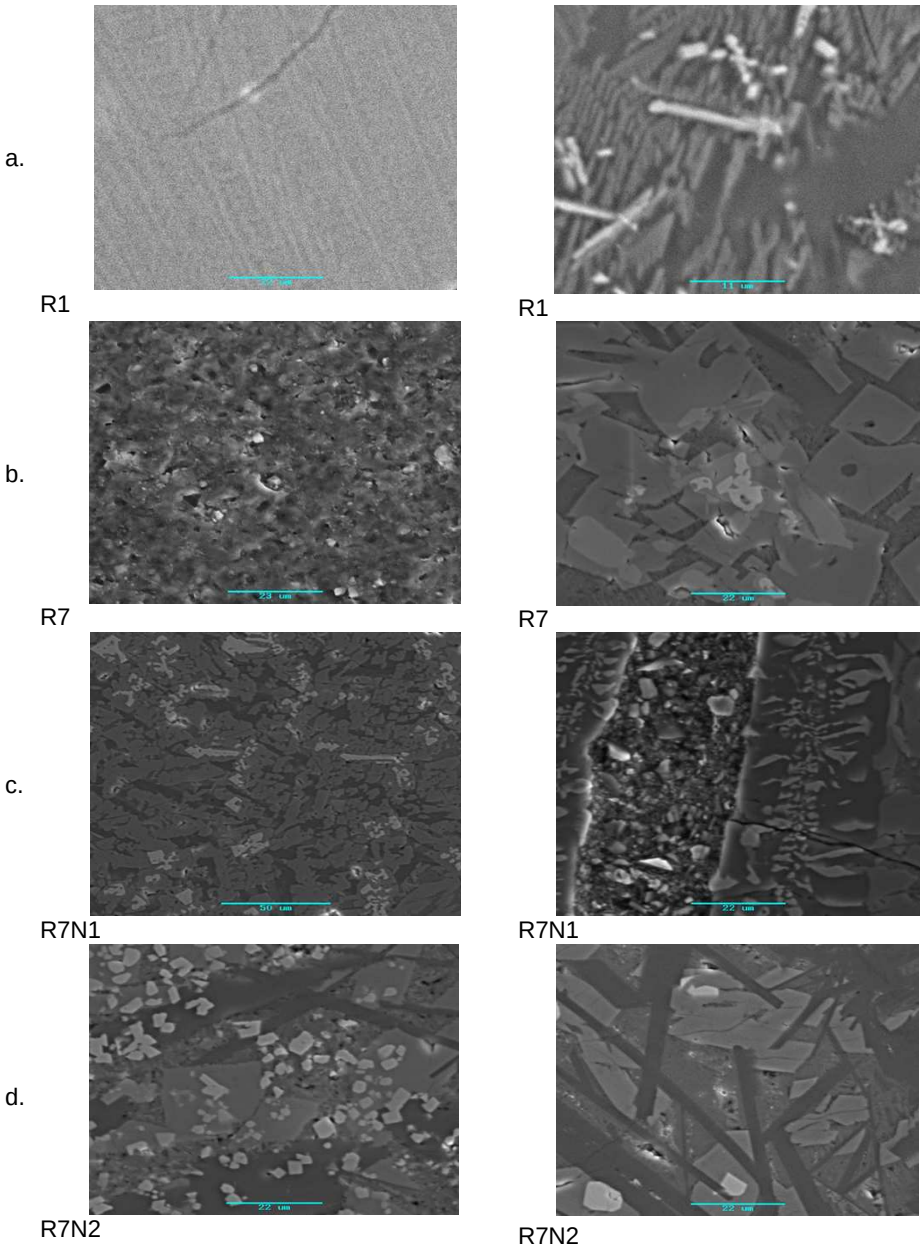
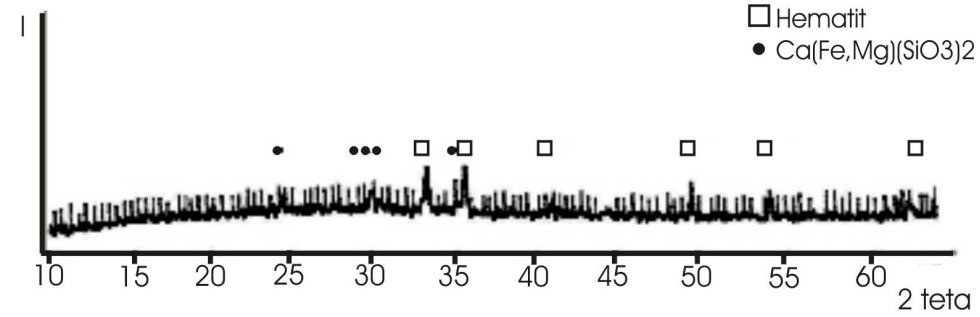


Figure 6. SEM images of the samples obtained through the second thermal treated
a – the R1 sample thermal treated at 850^{o}C – 10h plateau
b – the R7 sample thermal treated at 850^{o}C – 10h plateau
c – the R7 sample with TiO_2 nucleator thermal treated at 850^{o}C – 10h plateau
d – the R7 sample with Cr_2O_3 nucleator thermal treated at 850^{o}C – 10h plateau

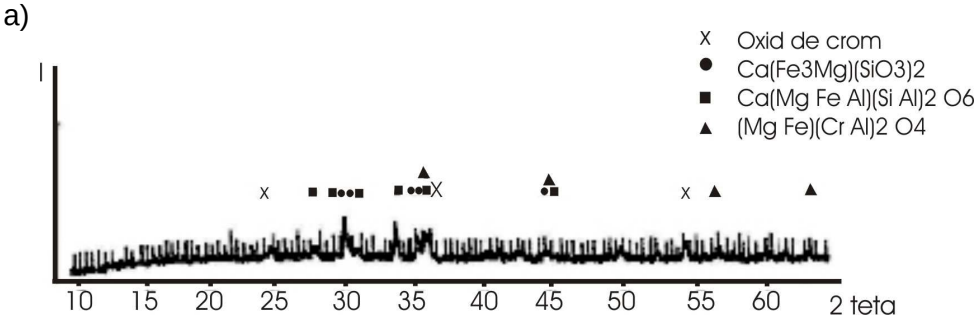
In order to identify the crystalline phases the R1N1 and R2N2 samples were analysed by X-ray diffraction (see Figure 7). Due to reduced crystal dimensions, the specific peaks can be noticed as very weak.

The crystalline phases, developed inside the vitreous matrix for both cases, are:

- in the TiO_2 samples: hematite and hedenbergite $Ca(FeMg)(SiO_3)_2$;
- in the Cr_2O_3 samples: ferous fassaite $Ca(Mg\ Fe\ Al)(Si\ Al)_2O_6$, magnesio-chromite with iron substitution $(Mg\ Fe)(Cr\ Al)_2O_4$, Cr_2O_3, as well as hedenbergite.



a)



b)

Figure 7. X-ray diffraction pattern for the samples R1N1 (a) şi R1N2 (b)

Conclusions

The present study emphasized the following conclusions:

- the Rovinari fly ash can be used to obtain crystallized glasses in the basic oxidic system SiO_2-CaO-Fe_2O_3;
- the crystallization tendency is more pronounced for samples with a higher ash content; moreover, the crystallization can occur without nucleation agents;
- the crystallization thermal treatment was applied in two ways: through heating with a plateau at 850℃ and through slowed cooling of the

melt and a plateau at the same temperature; the second was proven to be the most efficient;

- the crystallization phenomena are favoured when using TiO_2 and Cr_2O_3 as nucleation agents, thus producing two types of different crystals;

- immiscibility phenomena of the vitreous phases were observed through SEM analysis, especially for the Cr_2O_3 samples.

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