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BR95 33052

INIS-BR--3502

The Effects of Additives (MgO, La_2O_3 and Y_2O_3) in the Translucency of Alumina

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ABSTRACT

The effect of the addition of small amounts of MgO, La_2O_3 and Y_2O_3 in the optical characteristics of the high purity alumina has been studied. Specimens with high transmitance in the visible region has been obtained. High purity alumina powders have also been obtained through the crystallization of ammonium alum. Translucent samples have been produced from these powders.

INTRODUCTION

The translucent alumina has been widely used as envelopes for high pressure sodium lamps, which present a low electricity consumption [1]. For this application this material requires, besides transmitance, good mechanical and chemical properties. High translucency is achieved by the elimination of pores and by the absence of second phases which would actuate as light scatterers. Therefore, raw material purity and adequate processing condictions are essencial to obtain translucent samples.

It has been shown by Coble [2] that the sintering atmosphere is crucial to achieve full density. Total elimination of pores can only be obtained with hydrogen atmosphere or high vacuum. MgO is known to be the most efficient additive to inhibit discontinuous grain growth and for promoting sintering of alumina to high densities[3,4]. La_2O_3 and Y_2O_3 are also employed as

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additives to improve the transmitance of alumina[5], although their role has not been completely explained.

The synthesis of alumina from the crystallization of ammonium alum is an interesting process that employs salts as starting materials. In this process the final product has high degree of purity. The alum is prepared by dissolving the proper quantities of the reagents (aluminium and ammonium sulfates) in distilled water at an elevated temperature and allowing crystallization to occur slowly by cooling [6]. The resulting crystals can be redissolved and recrystallized and they will be purified during this process. This is a very simple and low cost process which is used in commercial plants for producing high purity alumina.

EXPERIMENTAL

Three commercial high purity aluminas were employed in the present work (Baikalox CR 6 from Baikowski Chimie, and AKP-3000 and AKS-3000 from Sumitomo Chemical Co.). MgO, La_2O_3 and Y_2O_3 were addicioned to these aluminas in different amounts. Table I shows the compositions prepared and respective denominations. The additive MgO was added as a solution of Mg nitride (analytical grade) and the rare earth oxides used were prepared in our Institute (purity: 98% La_2O_3 and 87% Y_2O_3). These materials were mixed in aqueous solution and dried using a freeze-drying technique in order to assure a good homogeneity of the mixture. The powder was then uniaxially pressed at 120 MPa using a 12-mm-diam. steel die. The densities of the samples were around 50 % of the theoretical density. The specimens were heat treated at 1000 °C for two hours in air and then sintered at 1815 °C under high vacuum (10^{-5} atm) also for two hours.

Polished samples (both sides) with 0,5 mm of thickness were measured in a spectrophotometer. In line transmitance measurements were carried out in the wavelength range from 400 to 2500 nm. After that the specimens were thermally etched in air at 1650 °C for 30 minutes and then sputtered with gold to be observed in a scanning electron microscope (SEM).

Adequate amounts of the ammonium sulfate and aluminium sulfate were dissolved under agitation in water at 80 °C before being filtered and rapid cooled. The ammonium alum produced by crystallization during 75 hours at 5 °C were separated and air dried for 24 hours. These crystals were redissolved in 1,6 liters of water and cooled as before. The crystals obtained in this second recrystallization were calcined at 1000 °C for 4 hours in an electrical furnace linked to an exhaustion system. The resultant alumina powder was finally calcined at 1250 °C for 3 hours. To this final powder wefe added 500 ppm of MgO and 300 ppm of La_2O_3 (composition ALU+5M3L) prior pressing, sintering and characterization (as described before).

Table I - Compositions prepared in this work and respective denominations.

ALUMINA	AMOUNT OF ADDITIVES (in ppm)	DENOMINATIONS
CR-6	500 MgO	CR6+5M
	300 La_2O_3	CR6+3L
	300 Y_2O_3	CR6+3Y
	500 MgO + 300 La_2O_3	CR6+5M3L
	500 MgO + 300 Y_2O_3	CR6+5M3Y
	300 La_2O_3 + 300 Y_2O_3	CR6+3L3Y
	500 MgO + 300 La_2O_3 + 300 Y_2O_3	CR6+5M3L3Y
AKP-3000	500 MgO	AKP+5M
	1000 MgO	AKP+10M
	500 MgO + 300 La_2O_3	AKP+5M3L
	1000 MgO + 600 La_2O_3	AKP+10M6L
	1000 MgO + 600 La_2O_3 + 600 Y_2O_3	AKP+10M6L6Y
AKS 3000	500 MgO (*)	AKS
ALU	500 MgO + 300 La_2O_3	ALU+5M3L

(*) as received

RESULTS AND DISCUSSION

Table II shows the chemical analysis, medium diameter and surface area of the materials investigated in the present work. All the powders are very fine and show high purity. It can also be noted that the alumina produced from the alum is comparable to the commercial powders. The chemical analysis of the additive materials is given in Table III. It can be seen that the yttrium oxide shows elevated amount of Ca. Further analysis using ICP-plasma showed that the concentration of La_2O_3 and Y_2O_3 (related to the total amount of rare earth) are 97.2 % and 86.0 % respectively. Thus the Y_2O_3 used in the present work showed elevated amount of others rare earth elements.

Figure 1 shows the transmitance curves of the sintered samples in the visible region and Table IV shows the transmitance values at 600 nm together with the apparent densities. The most striking feature of these results is the high translucence achieved with the CR6+5M3L, AKS-3000 and ALU+5M3L materials. These results indicate that the simultaneous addition of MgO and La_2O_3 lead to high transmitance of aluminas (compare sequence CR-6 and AKP-3000) although the highest value of transmitance obtained with alumina AKP-3000 (AKP+5M3L) is still inferior to the CR6+5M3L and ALU+5M3L. The values of transmitance obtained with the alumina AKS-3000 show that it is possible to produce materials with elevated translucency with the MgO-doped-alumina, although the transmitance value of the sample CR6+5M is still below to the best values obtained. An evaluation of the effect of the Y_2O_3 in the transmitance of the alumina is rather difficult since the yttrium oxide used in the present work has a high degree of the impurities. Further studies are been carried out to fully correlate the transmitance behaviour with the additives. Figure 2 shows photographs of the translucent samples.

Table II - Chemical analysis (in ppm), medium diameter (μm) and specific surface (m^2/g) of the powders studied.

element	CR-6	AKP-3000	AKS-3000	ALU
Cr	30	<10	10	15
Ni	10	<10	<10	
Zn	<20	<20	<20	
Si	40	20	30	50
Mn	1	<0.5	0.5	
Mg	25		>500	15
Cu	0.5	0.5	0.5	8
Na	50	<50	<50	100
Ca	50	<20	100	20
Ti	<20	<20	<20	
Medium Diameter	0.43	0.85	0.76	0.30
Specific Surface	2.3	4.7	4.5	9.5

Figure 3 shows a typical microstructure of a sample made from pure alumina (AKP-3000) with abnormal grain growth. Figures 4 shows the microstructure of translucent alumina (AKP+5M3L). This microstructure is very homogeneous and the few pores presents are located in the grain boundaries. Figure 5 shows the microstructure of the sample produced from the alum (ALU+5M3L). Although it shows high density and translucence, it also shows regions composed by small grains close together to the large ones. This could possibly be due to processing conditions, i.e., it is rather difficult to completely eliminate all the agglomerates (formed during the calcination of the powder) with pestle and mortar. The small amount of material produced in the present work does not allow the use of the appropriated milling.

Table III - Chemical analysis (in ppm) of the additives.

element	Mg nitrate	La oxide	Y oxide
Fe	200	75	75
Cr	<20	<45	<45
Ni	<20	<45	<45
Al	<20	<20	<20
Mn	<10	<15	<15
Mg	-	100	300
Ca	100	100	800
Si	150	-	-

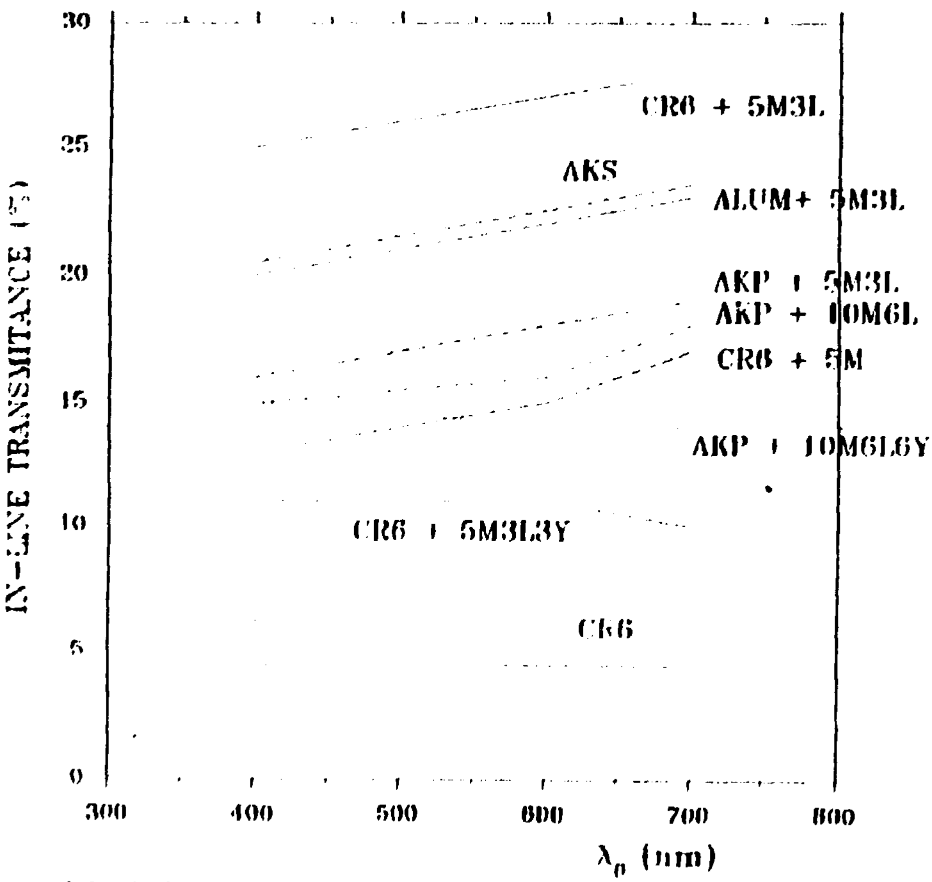

Figure 1 - Curves of the in-line transmitance for the visible region, obtained in this work.

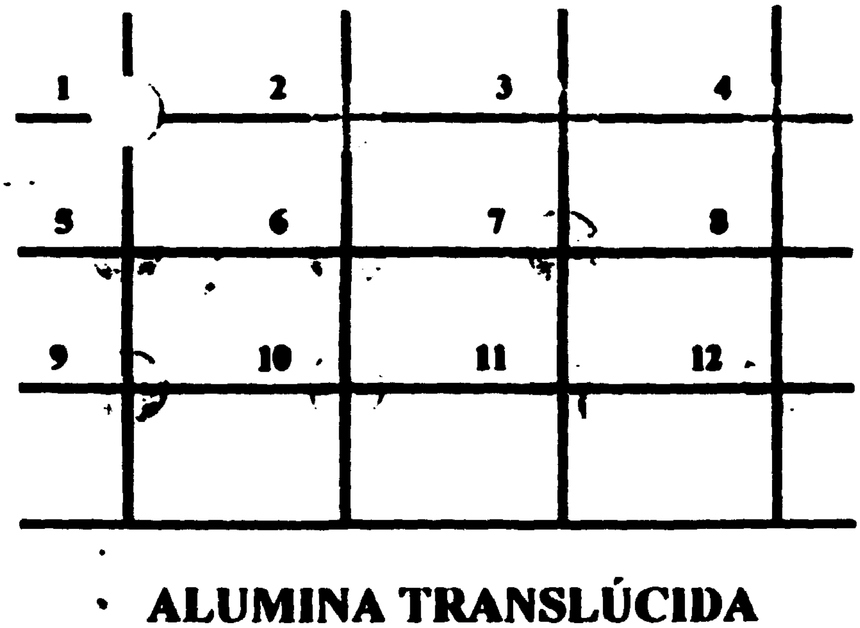

Figure 2 - Photograph of the translucent aluminas produced in this work.
1-CR10; 2-CR10+10M; 3-CR6+5M; 4-CR6+5M3Y; 5-CR10+5M3L3Y; 6-CR6+5M3L; 7-AKP+5M3L; 8-AKP+10M6L; 9-CR6+5M3L3Y; 10-A6+5M3L3Y; 11-ALU+5M3L; 12-AKP+10M6L6Y.

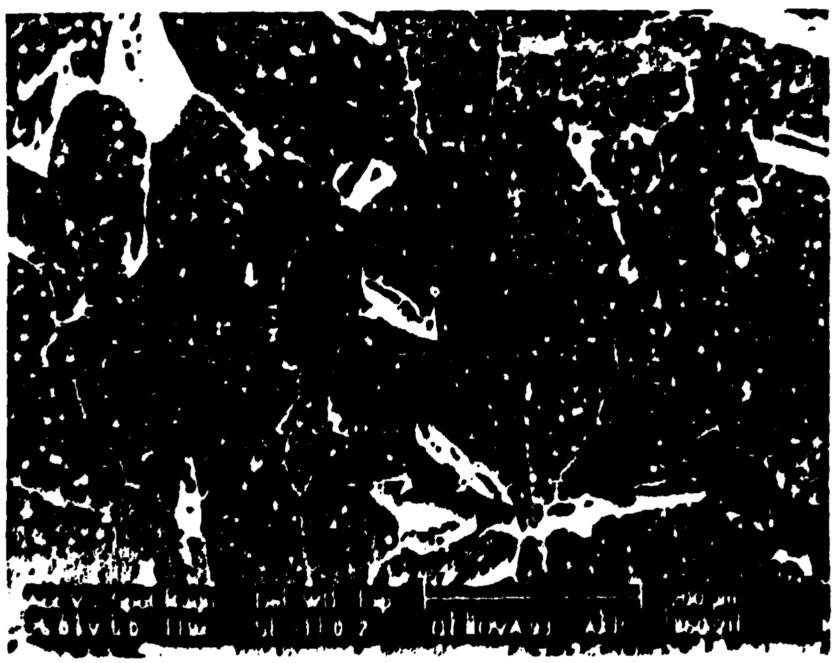

Figure 3 - SEM microstructure of the undoped AKP-3000, sintered at 1615 °C for two hours in high vacuum

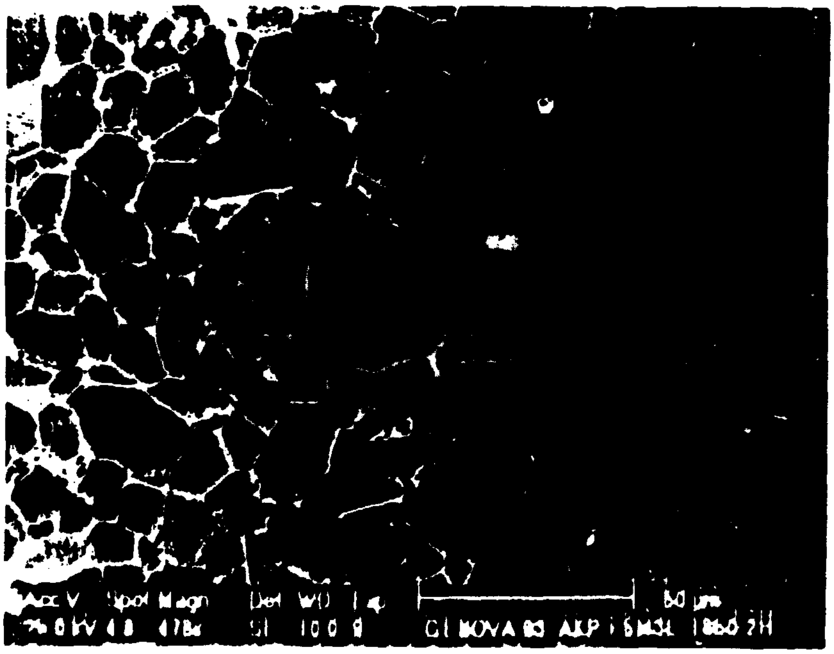

Figure 4 - SEM microstructure of the AKP+5M3L sample, sintered at 1815 °C for two hours in high vacuum

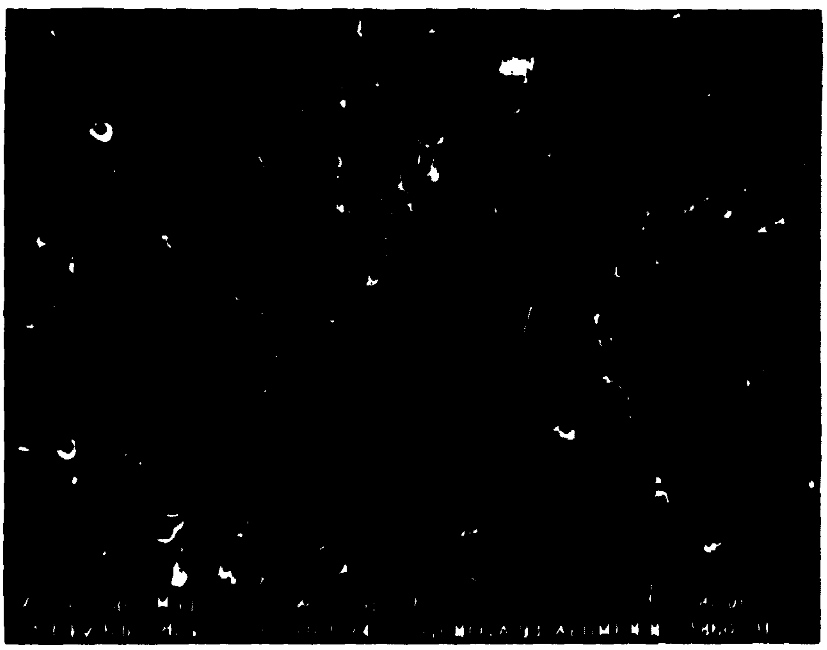

Figure 5 - SEM microstructure of the ALU+5M3L sample, sintered at 1815 °C for two hours in high vacuum

Table IV - Aparent densities and in-line transmitance for the samples produced in this work.

Composition	(%) ρ theoretical.	% of in-line transmitance λ_0=600 nm
CR6	98.52	4.5
CR6+5M	99.42	15.0
CR6+3L	97.01	opaque
CR6+3Y	97.59	opaque
CR6+5M3L	99.27	27.0
CR6+5M3Y	99.07	opaque
CR6+3L3Y	97.57	opaque
CR6+5M3L3Y	99.07	11.0
AKP	98.47	opaque
AKP+5M3L	99.52	18.0
AKP+10M6L	99.15	16.0
AKP+10M6L6Y	99.37	14.0
AKS	99.80	22.5
ALU+5M3L	99.22	22.0

CONCLUSION

The process to obtain alumina through the crystallization of ammonium alum yields a very fine and pure powder appropriated to the production of translucent alumina. The addition of 500 ppm of MgO and 300 ppm of La_2O_3 showed to be beneficial to obtain alumina with elevated transmitance. Studies are underway in an attempt to fully explain and correlate the effect these additives with the transmitance behaviour and the detailed microstruture.

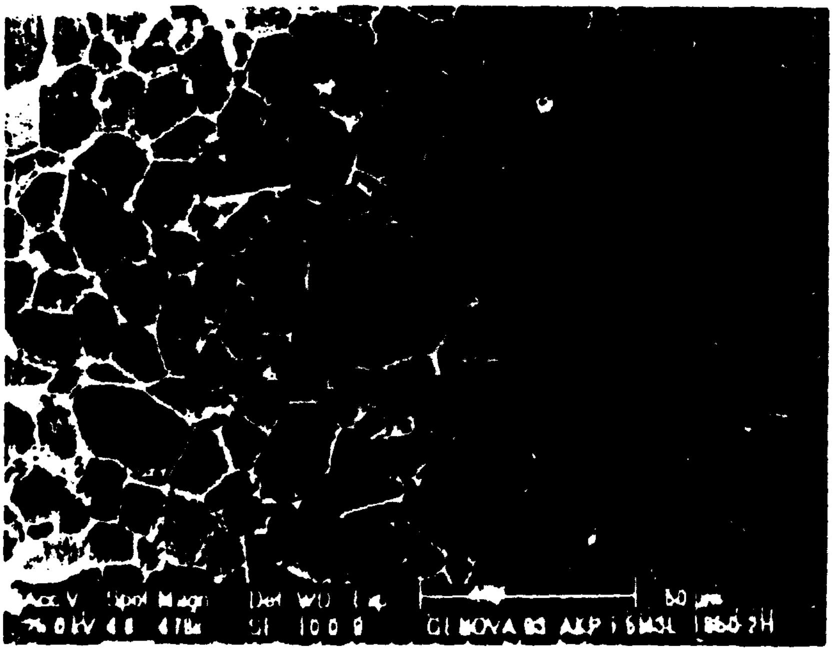

Figure 4 - SEM microstructure of the AKP+5M3L sample, sintered at 1815 °C for two hours in high vacuum

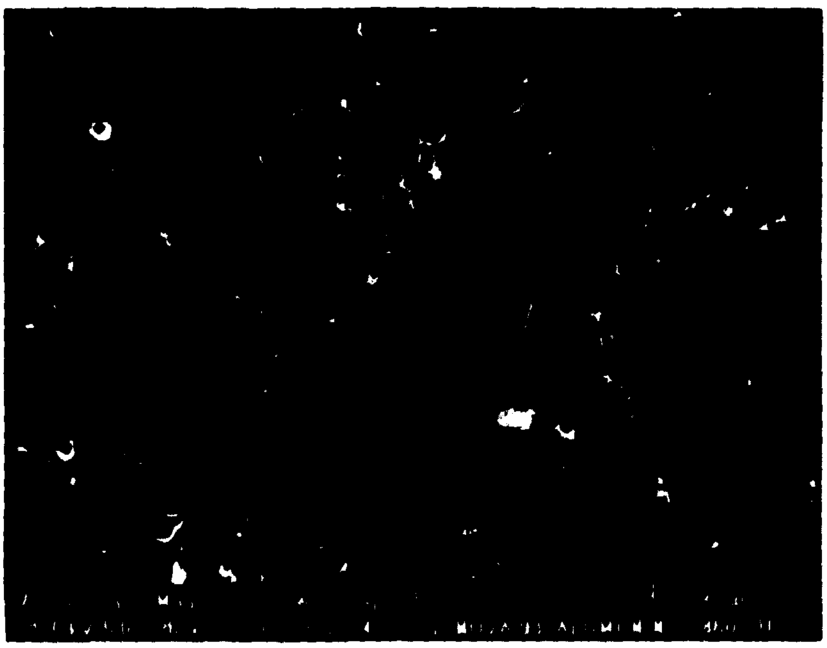

Figure 5 - SEM microstructure of the ALU+5M3L sample, sintered at 1815 °C for two hours in high vacuum

ACKNOWLEDGMENTS

Many thanks are due to the CNEN, FINEP and CNPq for the support of the research program of which this work forms a part. Thanks are also due to R. N. Faria for the assistance with the English version.

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Seminário

CAPACITAÇÃO TECNOLÓGICA EM MATERIAIS
19 de agosto de 1993

ALUMINA TRANSLÚCIDA E SUPERLIGAS A BASE DE NÍQUEL

Este seminário será realizado no âmbito do Programa de Cooperação Técnica, firmado em 15 de dezembro de 1992 entre a Japan International Cooperation Agency - JICA e o Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A. - IPT, na área de capacitação tecnológica em materiais. Este Programa tem como temas principais:

ÁREA DE CERÂMICA - DESENVOLVIMENTO DE ALUMINA TRANSLÚCIDA

Os produtos de alumina translúcida têm tido nos últimos anos aplicações crescentes, não só como componentes de lâmpadas de alta pressão de sódio, mas também para outras finalidades, como: sistema a laser, tubos de proteção de termopar para fornos de alta temperatura em atmosfera controlada, cadinhos para fusão de metais, bicos de pulverização, janelas para sistemas de microondas e infravermelho, peças para semicondutor e outras. Além disso, o conhecimento de sua tecnologia é extremamente útil para o desenvolvimento das outras cerâmicas a base de óxidos.

ÁREA DE METALURGIA - DESENVOLVIMENTO DE SUPERLIGAS A BASE DE NÍQUEL

As superligas a base de níquel têm um grande potencial para aplicação no Brasil na área de geração de energia, na forma de componentes de turbinas a gás (palhetas e direcionadores de fluxo), trabalhando em temperaturas superiores a 800°C. Este desenvolvimento permitirá o domínio da técnica de fabricação de componentes fundidos de superligas, a base de níquel, solidificadas convencional e unidirecionalmente.

PROGRAMA

08h45 - ABERTURA

09h00 - PESQUISA BÁSICA DE CERÂMICA TRANSLÚCIDA
- Yusuke Moriyoshi (National Institute for Research in Inorganic Materials - NIRIM/Japão)

09h55 - Intervalo para café

10h10 - APLICAÇÃO E SINTERIZAÇÃO DE CERÂMICA DE ALUMINA TRANSLÚCIDA
- Shunzo Shimai (Toshiba Ceramics Co./Japão)

11h25 - INFLUÊNCIA DE ADITIVOS (MGO, LA_2O_3, Y_2O_3) NA MICROESTRUTURA E TRANSLUCIDEZ DA ALUMINA
- José Carlos Bressiani (Comissão Nacional de Energia Nuclear - CNEN)

12h10 - Intervalo para almoço

14h10 - EFEITO DA VARIAÇÃO DOS PARÂMETROS MICROESTRUTURAIS SOBRE O ÍNDICE DE TRANSLUCIDEZ DA ALUMINA
- José Carlos da Rocha e Elza dos Santos Coelho (Instituto Nacional de Tecnologia - INT)

14h55 - MOLDES CERÂMICOS DE PRECISÃO PARA FUNDIÇÃO DE SUPERLIGAS
- Mario Boccalini Junior (Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A. - IPT)

15h40 - Intervalo para café

15h55 - PESQUISA E APLICAÇÃO DE SUPERLIGAS À BASE DE NÍQUEL
- Toshihiro Yamagata (National Research Institute for Metals - NRIM/Japão)

17h15 - Encerramento

IDIOMA: Inglês

TAXA: Gratuita

LOCAL: IPT/Auditório LAFER (Prédio nº 34)

INSCRIÇÕES: Vagas limitadas. Confirmar participação até 16/8/93.

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