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A Multi-Scale Approach of Degradation Mechanisms inside a SiC(f)/Si-B-C(m) Based Self-Healing Matrix Composite in a Dry Oxidizing Environment

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Abstract. Ceramic matrix composites are potential candidate to replace the nickel-based alloys in advanced aeronautic engines as in civilian ones. The durability of a SiC(f)/PyC(i)/Si-B-C(m) with a sequenced self-healing matrix and Nicalon fibers was investigated at low temperature. To better understand degradation mechanisms inside this composite, a multi-scale approach was chosen. Firstly, the oxidation behaviors of Nicalon fibers and the B₄C phase was studied under dry air at 550°C. Respectively, the whole composite was aged in similar oxidizing conditions. Correlation between these two levels leads to get an accurate description of degradation mechanisms inside a composite material and to evaluate the efficiency of the self-sealing process.

Keywords: oxidation, composite, Nicalon, boron oxide.

INTRODUCTION

Ceramic matrix composites such as SiC(f)/PyC(i)/SiC(m) consist in a SiC matrix reinforced with SiC fibers. These materials exhibit a low density and high thermomechanical properties, so they are potential candidate to replace the nickel-based alloys in advanced aeronautic engines as in civilian ones [1]. These composites display cracks due to their elaboration process, but also due to service conditions that include mechanical loading. These matrix cracks become an extended network for oxygen diffusion. The oxidation of the PyC weak interphase and the interfacial degradations can deeply occurs inside the composite. To limit this process, ceramic matrix composite SiC(f)/PyC(i)/Si-B-C(m) with a sequenced self-healing matrix have been developed and investigated. The introduction of boron in the matrix as B₄C phase allows the formation of an oxide at low temperature able to seal matrix cracks. To resume, the self-healing process consists in consuming part of incoming oxygen and limiting their access to the PyC interphase by sealing the matrix cracks with a liquid B₂O₃ oxide phase. Self-sealing processes have been investigated in previous works for similar materials at 600 and 1200°C [2]. In this work, the life time of a SiC(f)/PyC(i)/Si-B-C(m) composite was evaluated at lower temperature (550°C). In order to clarify the role of each element of the composite in the self-healing scenario, a multi-scale approach was chosen. In a first step, oxidation tests were performed on Nicalon fibers to extract their oxidation kinetic law and on the B₄C phase to characterize its role in the self-healing process at 550°C, and in a second one, the whole composite is oxidized to evaluate the efficiency of the self-sealing process.

EXPERIMENTAL PROCEDURE

Materials and Oxidation Chemical Reactions

The investigated material is the Cerasep®A40C manufactured by Snecma Propulsion Solide (SAFRAN GROUP). It is a woven-SiC-fibers reinforced Si-B-C sequenced matrix composite. This material is schematized in figure 1. The different matrix layers are crystallized SiC, and amorphous Si-B-C phases. The interphase is pyrocarbon. The sequenced matrix is reinforced by Nicalon SiC fibers (NLM207). Nicalon fiber is polycarbosilane-derived SiC fiber obtained by reticulation under O₂ and pyrolysis. They are manufactured by Nippon Carbon Co., Ltd (Japan) in the form of yarn with 500 fibers.

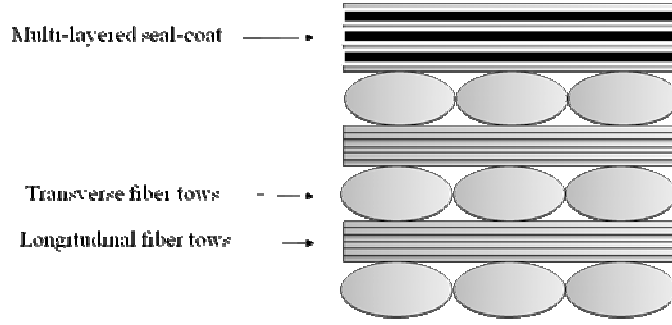


FIGURE 1. Schematic representation of the Cerasep®A40C composite

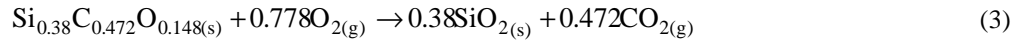
The oxidation behavior of silicon carbide under several oxidizing atmospheres has been widely studied in the literature. Nevertheless, for Nicalon NLM207 fibers, quantitative results have been reported only for relatively high temperatures ($\geq 700^\circ\text{C}$). To describe the oxidation mechanism of the Nicalon fibers, the growth of the silica scale is described by the equation 1 proposed by Deal and Grove [3]:

$$x^2 + Ax = B(t + \tau) \quad (1)$$

Where x is the thickness of the silica scale, τ is the initial thickness (often neglected), A and B are reaction constants. For sufficiently long time, the Deal and Grove model is simplified and the growth rate of silica is described by a parabolic law (equation 2), when the oxygen diffusion through the silica scale becomes the limiting step.

$$x^2 = k_p t \quad (2)$$

The mean composition of Nicalon NLM207 fibers after desizing is $\text{Si}_{0.38}\text{C}_{0.472}\text{O}_{0.148}$ [4]. Assuming that oxygen in the fiber participates in oxidation, the global oxidation reaction is (equation 3):



Boron oxide is a good candidate to seal matrix cracks by filling and flowing. Indeed, it exhibits a low melting point (about 460°C), and an appropriate viscosity. This oxide can be obtained by the oxidation of B_4C at low temperature ($< 700^\circ\text{C}$) according to the reaction 4.



The oxidation kinetic law of the B_4C phase has been established in previous studies by Garitte [5]. At low temperatures ($< 600^\circ\text{C}$) its oxidation kinetic of the B_4C phase (equation 5 and 6) is written as the thickness of consumed boron carbide and formed boron oxide for oxygen partial pressures ranging between 10 and 80 kPa.

$$k_p(\text{B}_4\text{C}) = 1.14 \cdot 10^8 \cdot \exp\left(-\frac{204000}{RT}\right) \cdot P_{\text{O}_2}^{0.9} (\mu\text{m}^2 \cdot \text{h}^{-1}) \quad (5)$$

$$k_p(\text{B}_2\text{O}_3) = 2.04 \cdot 10^9 \cdot \exp\left(-\frac{204000}{RT}\right) \cdot P_{\text{O}_2}^{0.9} (\mu\text{m}^2 \cdot \text{h}^{-1}) \quad (6)$$

Nevertheless, under dry air, this oxide volatilizes significantly above 900°C (equation 7).



Thus, B_4C is the main constituent inside the matrix that participates in the self-healing process at low temperature.

Samples and Oxidation Tests

In order to establish a scenario of degradation of the Cerasep®A40C composite material, the oxidation behavior of each component must be described. Thus, the oxidation kinetic rate of Nicalon fibers was determined and the oxidation behavior of the B₄C phase was investigated.

To extract the oxidation kinetic law of Nicalon fibers, oxidation tests were performed on 4 bundles of 5 centimeters long. Oxidation tests were carried out at temperatures ranging from 550 to 800°C during times between 100 and 500 hours.

To investigate the role of the B₄C phase in the self-healing process, polished-cross sections of composites were oxidized. The progressive formation of the liquid B₂O₃ phase was displayed and in particular, its ability to spread on the composite surface. This property depends on its chemical affinity with the different constituents and its viscosity. To prepare such a specimen, a thin slice of composite was cut, polished and oxidized.

The different oxidation tests were realized in a high temperature furnace at atmospheric pressure in dry air. The uniform heating zone of the furnace is approximately 200 mm long. During the ageing, materials were oriented parallel to the gas flow in alumina sample holders (purity: 99,7%). Samples were extracted from the hot furnace, cooled in ambient air and mass variation is measured. Then, they were again introduced in the furnace at the working temperature.

Materials Characterizations

After ageing, the thickness of the formed silica ring around Nicalon fibers was measured from observations by Scanning Electron Microscopy (SEM) (figure 2). For the measurement of the thinnest ones (≤ 50 nm), Auger Electron Spectroscopy (AES) with an Ar sputtering system was used.

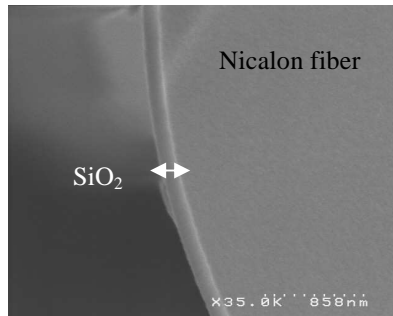


FIGURE 2. Silica ring on a Nicalon fiber after 408 h ageing at 600°C in dry air

On the oxidized composite specimens, observations by SEM with an Energy Dispersive Spectroscopy device (EDS), allow to determine the chemical composition of formed species and their repartition after exposure.

RESULTS

Oxidation Kinetic Law of Nicalon Fibers under Dry Air

As predicted by the Deal and Grove model, the evolution of silica thickness versus time follows a parabolic evolution. The activation energy was extracted from an Arrhenius plot (figure 3): 102 ± 12 kJ.mol⁻¹ in a gaseous mixture with an O₂ partial pressure of 20 kPa from 550 to 800°C.

In dry air, the oxidation kinetic law of SiC Nicalon fibers can be written for temperature ranging from 550 to 800°C by the following equation (written as the thickness of silica formed):

$$k_p = 8.14.10^7 \cdot \exp\left(-\frac{102000}{RT}\right) (\text{nm}^2 \cdot \text{h}^{-1}) \quad (8)$$

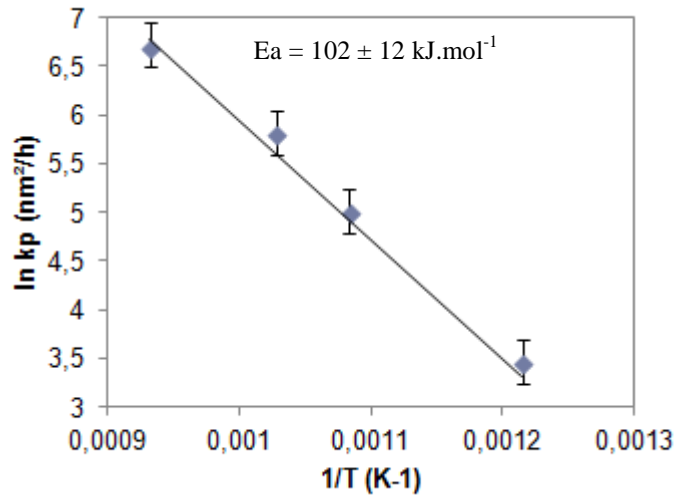


FIGURE 3. Arrhenius plot of the oxidation rates from 550 to 800°C for SiC Nicalon fibers in dry air (P_{O_2} : 20 kPa)

Formation Rate of B_2O_3 by Oxidation of B_4C

When a material is oxidized, it is partially consumed and only a low part of the whole formed oxide contributes to a volume expansion above the material (Figure 4(a)). Only this low part can participate to close a matrix crack and form a cork limiting further oxidation inside the composite. On the figure 4(b), the consumed thickness of B_4C and respectively the whole thickness of the oxide formed are reported with distinguishing the part leading to a volume expansion of the material. However, in the case of a liquid oxide formed, this protected oxide can flow and its thickness may not increase.

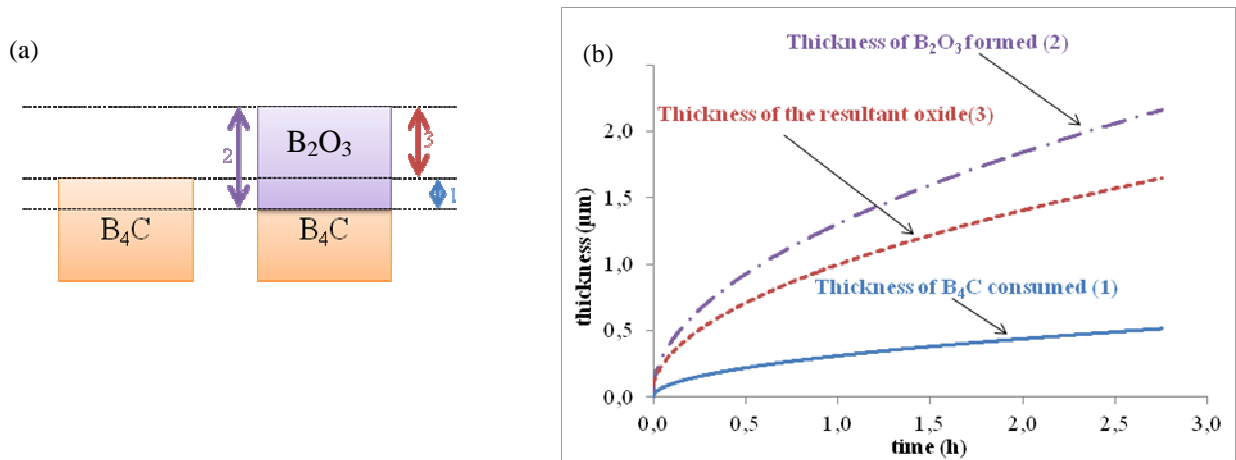


FIGURE 4. Oxidation of B_4C : (a) Schematic of thicknesses of consumed B_4C and formed B_2O_3 , and (b) Boron carbide and boron oxide thicknesses calculated at 550°C under an O_2 partial pressure of 20 kPa.

Oxidation of a Multi-Constituents Composite Material

From SEM observations on aged polished cross sections of composite, the B_4C layer appears as the most reactive constituent at 550°C. Indeed, others layers are not significantly oxidized with no morphologic modification compared to the B_4C phase. Energy Dispersive Spectroscopy analyses (EDS) confirm that boron oxide is the main oxide formed at this temperature and as expected, the thickness of boron oxide increases with time (figure 5).

It observed that B_2O_3 preferentially spreads on Nicalon fibers. This means that fibers are better wet by B_2O_3 than the SiC CVI matrix (figure 5). Along the cross section of the multi-layered seal-coat, on oxidized B_4C layers no oxide drop is visible (Figure 6) and B_2O_3 is not detected by EDS analyses. Then, B_2O_3 is supposed to spread on the seal-coat surface and formed a thin oxide film not detectable by EDS (the excess of B_2O_3 should flow out of the observed cross section along the side of the composite).

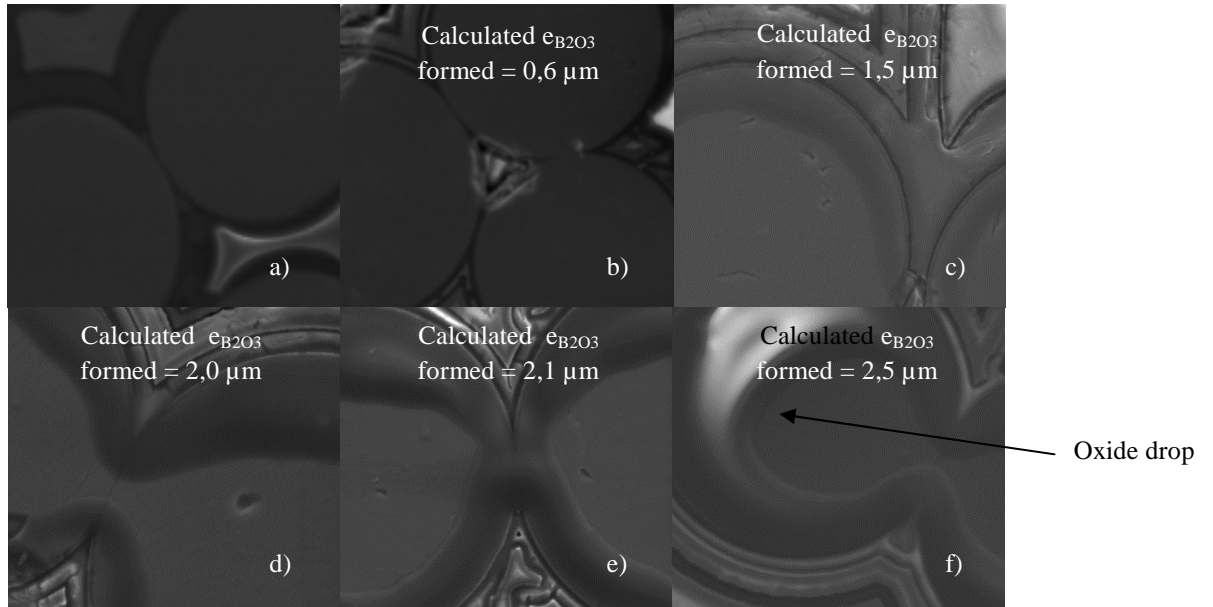


FIGURE 5. Polished cross section of the Cerasep@A40C specimen exposed at 550°C in dry air at atmospheric pressure for variable times: a) 0 min; b) 15 min; c) 75 min; d) 135 min; e) 165 min and f) 225 min.

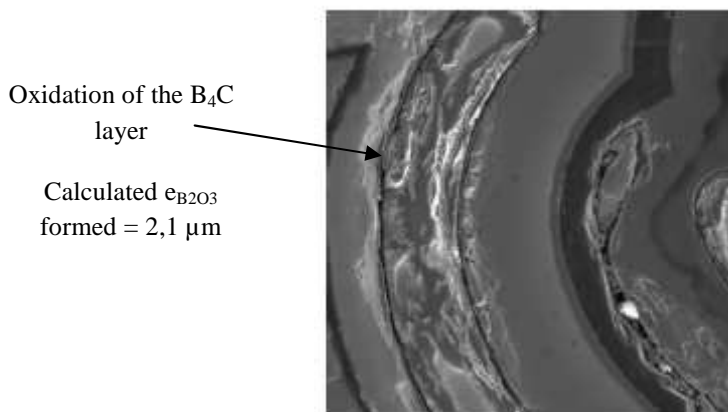


FIGURE 6. Polished cross section of the Cerasep@A40C specimen exposed at 550°C in dry air at atmospheric pressure for 165 min.

Oxidation of Dog-Bone Composite Specimens

Respectively, pre-damaged dog-bone composite specimens are aged at 550°C at atmospheric pressure in dry air and the weight changes are punctually measured.

Only a very low variation is recorded during the oxidation of Cerasep@A40C composite after exposures for 300 hours (< 0,01 %) (Figure 7).

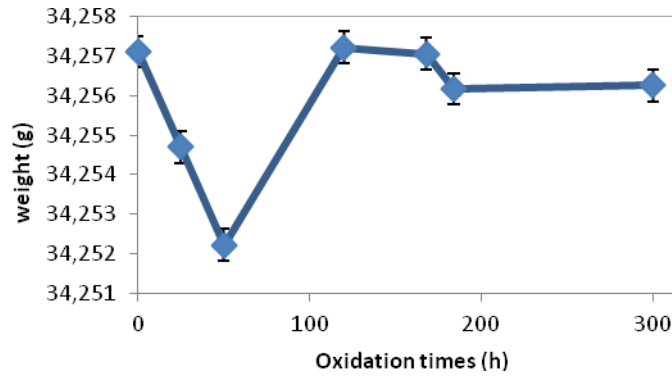


FIGURE 7. Mass variations recorded during the oxidation of the dog-bone composite under dry air at atmospheric pressure at 550°C.

DISCUSSION

Oxidation Kinetic Law of Nicalon Fibers under Dry Air

The oxidation kinetic law of Nicalon fiber established in this work has to be compared to data obtained from others works at higher temperatures from the literature [4]. Huger et al. realized oxidation tests on Nicalon fibers at temperatures higher than 700°C, but no kinetic law has been extracted. He gave an activation energy of 80 (± 60) kJ.mol⁻¹. Furthermore, a linear domain is mentioned for short exposure times (< 10 hours) at 700°C. However, Huger realized his tests in ambient air, and moisture is probably present. Indeed, H₂O leads to increase the SiO₂ layer permeability by formation of Si-OH chemical bonding [6]. With this increase of the layer permeability, the linear domain is extended. On the contrary, a linear domain is not highlighted in our work. Indeed, in this latter domain, at low temperature the involved mass variation are too low to be accurately recorded. The measured thickness of the silica scale by SEA with an Ar sputtering system doesn't allow to conclude on the linear or parabolic evolution of the initial oxide growth rate in this work.

The Self-Healing Process

Observations of cross sections of oxidized composites show that at 550°C under dry air, boron carbide is the main constituent consumed and boron oxide is the oxide formed with the capability to seal a matrix crack. At 550°C, due to the high oxidation rate of carbon, the low mass loss recorded during the first 50 hours of oxidation (figure 7) can be related to the oxidation of the carbon interphase, before the establishment of the protection by B₂O₃.

During the self-healing process, B₂O₃ preferentially spreads on the Nicalon fibers and tends to flow along the seal-coat multilayered. Indeed, at 550°C, under dry air, the contact angle between B₂O₃ and the different constituents of the seal-coat is lower than 90° (figure 8) that prove the good glass wettability.

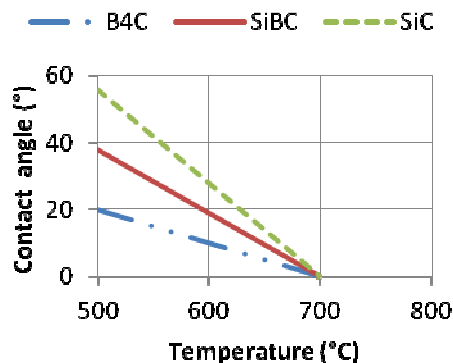


FIGURE 8. Contact angle between liquid B₂O₃ and SiC, Si-B-C and B₄C specimens in dry oxygen for temperatures ranging from 500 to 800°C [7]

Moreover, the viscosity of the B_2O_3 oxide for temperatures ranging from 600 to 1100°C allows the formation of sealant thin film [8], and from the results obtained in this paper show that this property can be extended below 600°C, at least up to 550°C. Hence, an oxidation scenario is proposed in the figure 9.

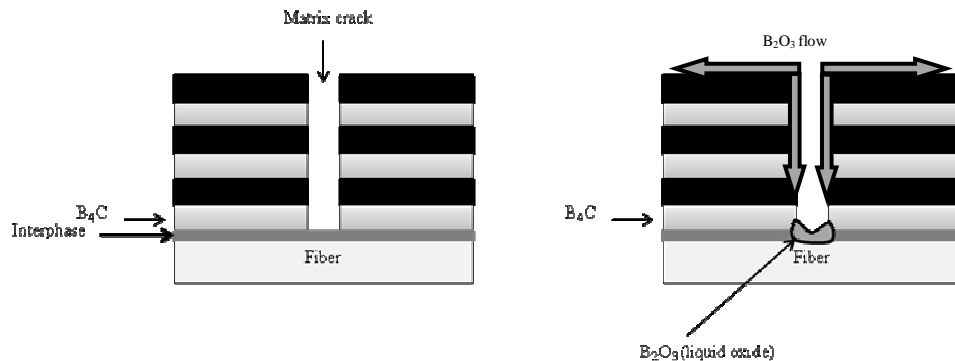


FIGURE 9. Schematic of the oxidation process inside a self-sealing matrix crack at 550°C under dry air at atmospheric pressure

CONCLUSION

A more accurate description of the oxidation behavior of the Cerasep®A40C is proposed at 550°C under dry air using a multi-scale approach: the first level is the oxidation rates of the fibers and the B_4C phase, and the second one is the oxidation of the whole composite. It is shown that the self-healing process is efficiency at 550°C and matrix cracks are sealed. Complementary analyses will be done, and especially on the dog-bone composite oxidized to clarify the oxidation progression through a pre-damaging crack. Post-exposure mechanical test must be lead to predict the durability of the CMC. Eventually, corrosion tests will be performed to take into account the B_2O_3 volatilization in a wet atmosphere. Thus, the B_2O_3 formation will be compare to the B_2O_3 rate to estimate and foresee the self-sealing efficiency.

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REFERENCES

1. R. Naslain and F. Christin, *MRS bulletin*, 2003, pp 654-658.
2. L. Quémard, "Corrosion à haute température et à haute pression de composites thermostructuraux à matrice séquencée SiC/[Si,C,B] et C/[Si,C,B] pour applications aéronautiques ", PhD Thesis, Université de Bordeaux 1, 2005.
3. Deal and A.S. Grove, *Journal of Applied Physics*, 1975, pp 3370-3378.
4. M. Huger, *Journal of Materials Science Letters*, 1993, pp 414-416.
5. E. Garitte, "Etude de l'oxydation/corrosion des composites céramiques", PhD Thesis, Université de Bordeaux 1, 2007.
6. E.J. Opila, *Journal of American Ceramic Society*, 1999, pp 625-636.
7. S. Wery, "Etude de la réactivité de composites à matrice céramique à haute température", PhD Thesis, Université de Perpignan, 2008.
8. A. Napolitano, *National Bureau of Standard*, 1965, pp 613-616.