EasyChair Preprint

№ 283

Failure Analysis of Black Spot On Non Ferro Tableware Ceramic Surface

Oscar Haris, Iman Sukirman, Umar Syahrul, Dikko Mahardika and Puji Aditia Pratama

June 19, 2018

Failure Analysis of Black Spot On Non Ferro Tableware Ceramic Surface

1st Oscar Haris, 2nd Iman Sukirman, 3rd Syahrul Umar, 4th Dikko Mahardika, 5th Puji Aditia Pratama
1st *Department of Mechanical Engineering,* 2nd,3rd,4th,5th *Departement of Mechanical Engineering*
Nusa Putra University
Sukabumi, Indonesia
oscar.haris@nusaputra.ac.id, syahrul.umar@nusaputra.ac.id, sukirman@nusaputra.ac.id, dikko.mahardika@nusaputra.ac.id, puji.aditia@nusaputra.ac.id

Abstract — **Indonesia has a quite large source of natural materials in the form of SiO_2, AL_2O_3, CaO, MgO, K_2O, Na_2O which can be used as raw material for ceramic manufacture. Ceramic is material non-metals that have different characteristics and particular advantages with other materials which often cause failure on end product of ceramic, especially on ceramic tableware, with their black spot defect on its surface. Black spot failure that occurs on the surface of ceramic tableware can be seen from visual identification of defects in biscuits and white body. The failure analisys is using root cause Fault Tree Analisys (FTA), equipped with a variety of SEM and XRD material characterization testing. From the results of SEM and XRD material characterization test, the black spots derived from any element of Fe-based according to white body product SEM/EDS test, whereas for ceramic raw materials after XRD test not obtained the compounds Fe on the raw material, however obtained alluminum Iron Carbida compound in biscuit products. The conclusion of the black spots failure analisys on the surface of ceramic tableware ceramics is derived from the production process itself.**

Keywords - Black spots, SEM / XRD, Failure Analisys

1. INTRODUCTION

Indonesia has amount of natural resources material in the form of SiO2, Al2O3, CaO, MgO, K2O, Na2O which can be used as raw material ceramic manufacture. The ceramics industry initially considered as preservation of the cultural wisdom, but in its development of ceramic industry in Indonesia is increasing, has became one of the driving wheels of reliable national economy, which held quite extensive market, both in the domestic and international level. The ceramics industry has vary products such as traditional ceramics and modern ceramics. Traditional ceramic produces products such as tableware, tiles, pottery, tile and others, while the yield of modern ceramic produces such as ceramic electrical insulators, ceramic fuse, ceramic medical equipment and others.

Ceramics is one of the non-metals material that has different characteristics and specific advantages with other materials. Ceramic crystal structure consisting of various different sizes of atoms or minimum consist of two types of the most complex elements of all the material structure. The bond between these atoms is generally covalent or ionic, so this bond is strong. This bond is much stronger than a metal bond. Therefore, ceramics significantly has characteristics such as hardness and heat resistance and electrical, higher than metal. Ceramics can be bonded in the form of a single crystal or polycrystalline. The particle size has a great influence on the strength and characteristic of ceramics.

Tableware ceramics should be produced safe for use, the tableware company should be always maintenance visual product quality to attrack the customers . Therefore company apply ISO 9001 standarization since 2008. Deffect that occure does not fulfill material compotition standart such as black spot, bubble, and refiring is the product does not have a standard composition until the end of the process [1]

II. LITERATURE REVIEW

Ceramic materials consist of a complex phase which is a compound of metal and non-metal elements that are bonded ionic or covalent. Ceramics generally have a crystalline structure and a bit of free electrons. Ceramic chemical composition comprising an assortment of simple compounds up to a complex mixture of several phases.

In the manufacturing ceramic is know the body of ceramic triaxial, is ceramics made of three material compotition , plastis material (clay), filling material (kwarsa) and melted material (feldspar) [2]. And the types of ceramic base material consists of :

A. Kaolin

Kaolin is a natural mineral which is one type of clay which is primarily composed of mineral kaolin. This type of clay is canescent. In nature kaolin is derived from the decomposition of feldspar. As the mineral, kaolin mixed with other oxides such as calcium oxide, magnesium oxide, potassium oxide, sodium oxide, iron oxide, and others [3]. Kaolin types commonly used in the manufacture of ceramics are AKS 18, AKS 88, AKS 90, AKS 96, LCK LCK 60 and 70. Each kaolin has a distinctive character that is as varied as the level of plasticity, green strenght, and the value of whiteness [4].

The main function of kaolin in ceramic body formation is to control the firing range and distortion during combustion, kaolin will form the first liquid phase in the system at a temperature of about 9000 ^{0}C, then the next and the main crystalline phases mullite .

B. Bentonite

Bentonite is a term in clay containing monmorillonit in world trade and includes dioktohedral group. Naming types of clays depend on inventors or researchers, for example, geologist, mineralogy, mineral and other industries. Bentonite can be divided into two groups based on the content of the hydrous aluminum silicate, which is activated clay and fuller's Earth. Activated clay is clay that lack power to pale, but it can be improved through processing. Bentonite also include the type of secondary clay (sedimentary) which is highly plastic and fine-particled used to add plasticity of ceramic body. Bentonite is alumina silikat hidrat mineral as the part of pilosilikat or layered silica consist of tetrahedral tissue $(SiO4)_2$ intertwined in unlimited room so it's formed anion tissue $(SiO3)_2$. Bentonite chemical formula is $Al_2O_3.4SiO_2.H_2O$. 85% of bentonite content is montmorilonit[5]. Bentonite can expand to 8-15 time if dipped in water and fixed dispersion at several time in the water. Except montmorilonit content is bentonite is baidellite with chemical formula Mx $(Al_4$-xMgx) Si_8 O_2 $(OH)_4$ NH_2O [6]. Bentonite is part of monmorilinit clay types derived from the weathering of volcanic rocks. To increase the plasticity of clay. Bentonite characteristics are highly plastic, fine-particled, has melting point to 1200 ^{0}C.

C. Silica

Silicon dioxide is also known as silica (from the Latin silex), is a silicon oxide with the chemical formula SiO2 which has been known of its hardness since ancient times. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. Silica produced in several forms, including fused quartz, crystal, colloidal silica, silica gel, and aerogel. Silica is a chemical compound with the molecular formula SiO2 (silicon dioxsida) which can be obtained from the silica mineral, vegetable and synthetic crystals. Silica is a mineral compound commonly found in mineral / quarry in the form of minerals such as quartz sand, granite, and fledsfar containing crystals of silica (SiO2) [7].

D. Aluminum Oxide (Al_20_3)

Aluminum oxide (alumina) is a chemical compound of aluminum and oxygen with the chemical formula Al_2O_3. By nature, alumina composed of the mineral corundum. These compounds included in application material group, has properties that strongly support its use in a variety of allotment. These compounds are known to be a good electrical insulator, so it is widely used as a high temperature insulator material, because it has a large heat capacity[6]. Other character of alumina which supports application is the corrosion resistance[15] and a high melting point, which reached 2053 ^{0}C. In alumina glaze serves to control and compensate for melting and give strength to the ceramic body and glaze, while in the ceramic body to increase the viscosity, melting point, prevents crystallization and stabilizing the glass mass. In the plastic mass of ceramic, kaolin element will provide Al_2O_3 but not pure enough whereas plastic ball clay will provide Al_2O_3 but not pure plastic.

Alumina (Al_2O_3) is a non-silicate ceramic material that is most important, this material melts at a temperature of 2051 ^{0}C and retains its strength even at temperature of 1500 ^{0}C to a temperature of 1700 ^{0}C. Alumina has a high electrical resistance and resistance to thermal shock and corrosion. Alumina obtained from the processing of bauxite ore containing 50-60% Al_2O_3; 1-20% Fe_2O_3; 1-10% silica; little titanium, zirconium, and other transition metal oxides and the remaining 29-30% is water.

E. Feldspar

Feldspar is produced from weathering granite and lava rock, where clay was formed, feldspar including alumina silicate compound containing one or more elements such as: K, Na, Ca. As a material which is not plastic, feldspar is very important in the ceramic industry because it is able to reduce shrinkage during the drying process, and as a flux (melting) at a temperature above 1200 ^{0}C. Melting point between 1170 ^{0}C – 1290 ^{0}C. Feldspar is very useful in the manufacture of ceramics glassware, stoneware, porcelain, as well as materials to make the glaze. From the elements, feldspar contains material alumina (Al_2O_3), silica (SiO_2), and fluxes (K_2O or Na_2O), containing potassium (K_2O) is usually used to make the fine body ceramic because it is very active dissolving quartz, shaping very thick glass, and as fuser either in the body of fine ceramics so that the body of ceramic into a solid without changing its form (deformation), moderate contains a lot of sodium (Na_2O) to make a glaze. From the composition can be seen that the feldspar structure is not different from the structure of the clay, a natural silicate, pink or brownish and is a ceramic with a mineral composition is $NaAlSi_3O_8$. Feldspar is also a silicate texture and one of four silicon atoms replaced by aluminum atoms. At temperature above 900 ^{0}C feldspar generally remains stable and does not undergo a phase change.

F. Ceramic Fabrication Flow Process

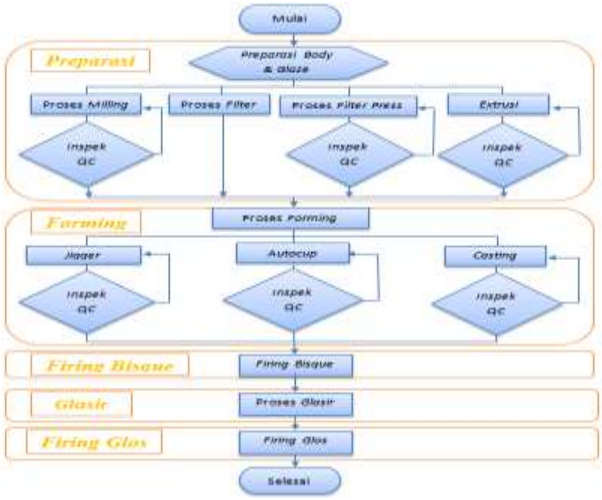

Fig. 1. Ceramic fabrication flow process

III. Research Methodology

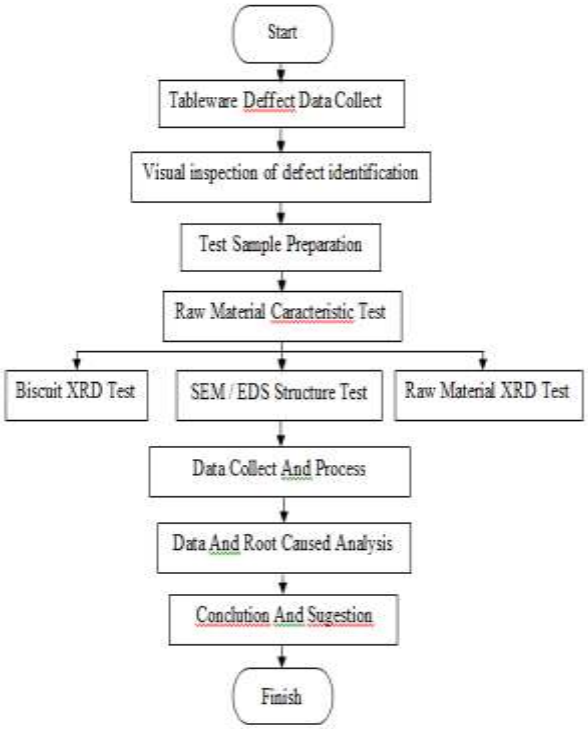

Fig. 2. Flowcart Research

A. Tableware Deffect Data Collect

Stages of data collection is done as a reference in determining the percentage of defects final results of ceramic tableware production. From this data will be concluded which defects are the most influential in achieving grade quality is directly related to the profit of ceramic tableware industry, so that the most dominant defect that will be targeted for research. Defects generated in the production process of ceramic tableware very many kinds, each of these defects can be classified by process, material, firing, and environment. The summarized defect data is taken during past one year, as reference to this research step.

B. Visual Inspection of Defect Identification

After collecting data of defect in the ceramic tableware industry, the next step is to do the visually identification of black spots defects. Black spots defect occur on the surface of ceramic tableware in a place that is never unexpected, that means the position of the occurrence of defects of black spots could be anywhere, can one point, two points, three points even across the entire surface of ceramic tableware, visual inspection is also include how much and how deeply flawed the black spots on the surface of ceramic tableware.

C. Root cause analysis (Fault Tree Analysis)

At this stage will be the search root of the problem by using the FTA to search for possibilities causes black spots on tableware, to perform the proper precautions to minimize the possibility of the occurrence of black spots and prevent it. Root cause analysis from the FTA result will be as a reference in proposing better and more efficient improvements for the productivity and quality of ceramic tableware.

FTA method describes the process (sequence), the cause of the failure (fault), that involved in the events, based on the mechanism of its production process, so that the causes of the dark spots can be analyzed and identified. Research using FTA methode must first understand the symbols. FTA started from loss or unintended consequences as the top event or head event, then identify all the factors and stages events that may contribute to a top event.

D. SEM /EDS Microstructure Test

This test method is done against the black spots in the white body surface to be able to recognize the microstructure, surface topography that is characteristic of surface and texture (hardness, light-reflecting properties, and so on). Morphology is the shape and size of the object composer particles, to determine quantitative data composition of elements and compounds contained in the object, any compound that causes black spots. SEM testing is aimed to obtain information kristalograpi, which is information regarding the composition of the grains in the observed object (conductivity, electrical properties, strength, and so on). SEM has an enlargement up to 300,000 times. This test will be conducted at the Center of Regional Polymer Teknology Puspiptek Serpong Tangerang, this test is performed on the surface / wall of ruptured white body which contained black spots. The working principle of SEM stems from electron beam generated by filament on electron gun. In general, the electron gun used was a tungsten hairpin gun with tungsten filament coil form that function as the cathode. Stress is applied to the coil for resulting warming. The anode will form a force that can pull electrons drove towards the anode.

E. XRD Microstructure Test

Characterization of the crystal structure is one of the supporting characterization of the study, to be able to determine the crystal structure and phases which is formed in the raw material, biscuits dan white body. This process is done using Difragtometer sinar-X (XRD). In samples of raw materials test, biscuits and white body material is cut using ceramic cutting tools. The sample is placed on the holder, pressed using a glass with just enough pressure so that the sample does not shift or fall during the process, then inserted into the XRD box and ready to be characterized. This characterization is conduct in order to determine the structure of the crystal, the lattice parameters, and the formation of the ceramic layer. This characterization process is carried out in the Department of Materials and Metallurgy, University of Indonesia.

IV. Result and Discussion

A. Tableware Defect Data Collection.

Table, Data of top three defect of tableware ceramic production on PT. X year 2016

No	Month	Target			Value Pcs			Value %		
		Black spot	Porosity	Pin Hole	Black spot	Porosity	Pin Hole	Black spot	Porosity	Pin Hole
1	Januari	4.00	2.00	1.70	13050	5697	959	7.31	3.19	0.54
2	Februari	4.00	2.00	1.70	12578	3984	706	8.65	2.73	0.48
3	March	4.00	2.00	1.70	15890	4475	1176	10.09	2.84	0.75
4	April	4.00	2.00	1.70	17144	4840	2206	9.59	2.71	1.23
5	May	4.00	2.00	1.70	21146	4911	3251	12.51	2.91	1.92
6	June	4.00	2.00	1.70	18954	4822	3693	9.48	2.36	1.81
7	July	4.00	2.00	1.70	13598	4068	2642	9.71	2.91	1.89
8	August	4.00	2.00	1.70	16224	4203	2911	10.10	2.62	1.80
9	September	4.00	2.00	1.70	14654	4030	2509	8.95	2.47	1.53
	Avarege				14361.80	4103.00	2.065.30	8.64	2.47	1.28

B. Visual Inspection of Defect Identification.

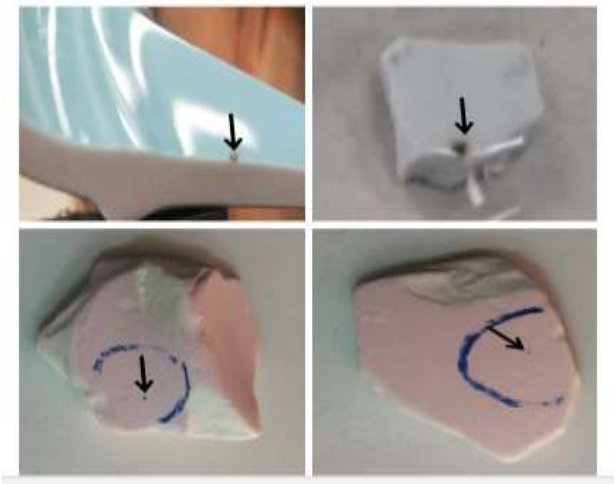

Fig 3, Black spot on White Body dan Biskuit surface

From the results of visual observation, it can be obtained by several identification related to the black spot defects, such as:

1. The appearance of black spots occur on the surface of the ceramic biscuit dan white body.
2. Black spots that appear on the surface lies in glazing layers, and layers between the glazing and body.
3. Black spots morphology structure do not have specific patterns.
4. The form of black spots color density level is not always the same between one and the other.
5. Black spots formed is always flat with the surface of the ceramic itself.
6. In the ceramic surface sometimes black spots may occure more than one point.
7. The black spots are formed so compounding with the ceramic surface, so it is very difficult to be removed.

D. Sample Test Preparation

Tests were carried out as supporting data in order to determine the failure of the black spots on the tableware ceramic using SEM / EDS micro-structure testing. Samples that tested is taken on the surface of white body with black spots. The process of extraction is carried out by rupture the white body which contain the black spots, The sample will be a SEM / EDS test reference, to determine the composition of the surface elements of the black spots and the formation of surface morphology.

Fig 4, Black spot sample test on tableware ceramic

E. SEM /EDS Test Result Data.

Fig 5, Foto *Scanning Electron Microscope* with enlarged 20.000 x indicates black spots in three area

F. XRD Test Result Data

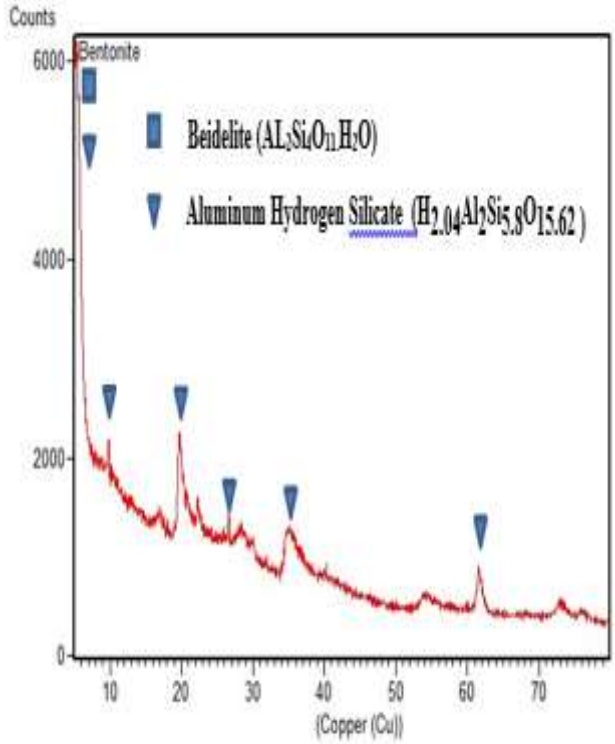

Fig 6, Bentonite XRD result

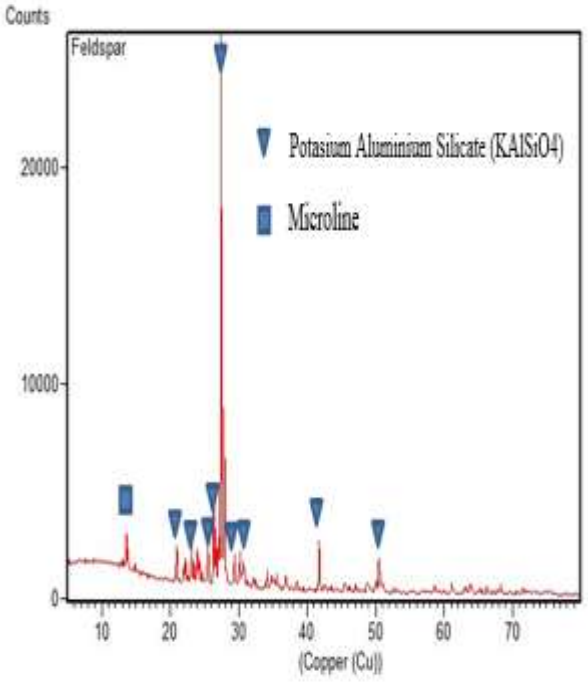

Fig 7, Feldspar *XRD* result

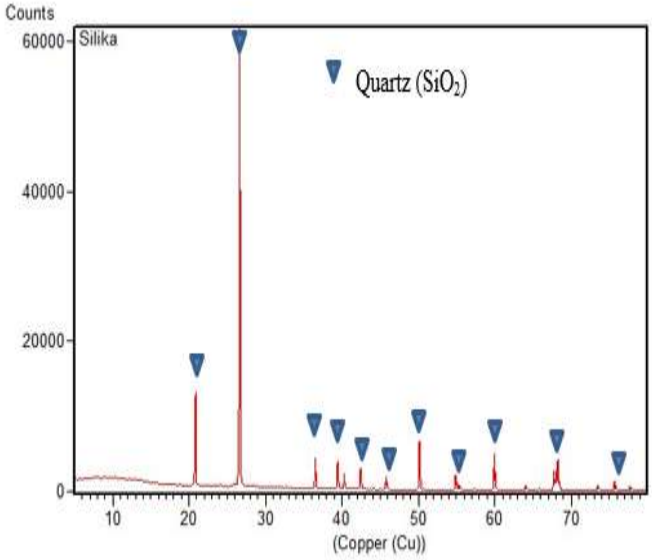

Fig 8, Silica XRD result

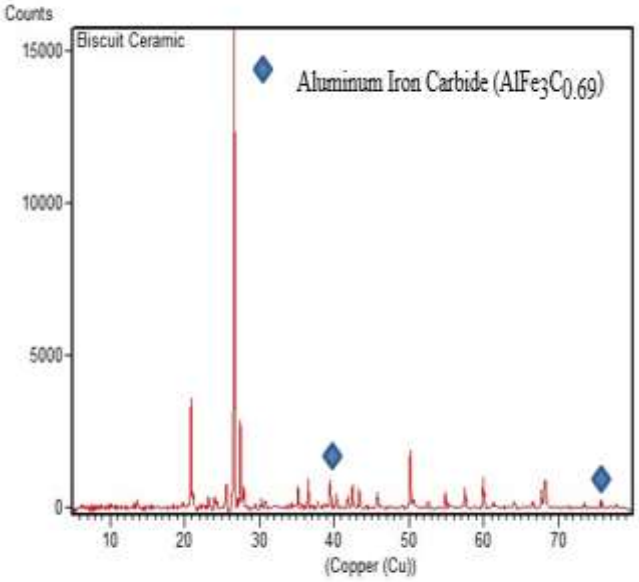

Fig 9, Ceramic biscuits *XRD* result

G. Discussion of Test Data Analysis Results.

Based on the data obtained from the testing of SEM / EDS for black spots on the surface of tableware ceramic, the analysis of test data are ceramic pieces with black spots on the outcome of the Scanning Electron Microscope (SEM) on the surface with black spots as seen in image 4.9. SEM image shows clearly the three-point area of black spots. The three point of the overall area, the core forms a triangular surface, in the first area of the core of a surface morphology is a triangular shape, with a flat topography ceramic material surface itself, the position of the formation of the glazing layers of colors is so thick and lustrous, form a dense color influenced the

composition of its form of elements, while the second area of the core of a triangular-shaped surface morphology also with relatively smaller dimensions than the first area. Similar to the first area, the location of the surface topography was flat with the ceramic material itself, lies in glazing layers, with colors that are not so concentrated, while the third area of the core forms a triangular surface with a relatively smaller size than the first and second areas as well as with the concentration of color is so intense, not much different as the first area, the location of the surface topography was flat with the ceramic material itself, lies in glazing layers.

EDS Test Analisys Result Data

Table of forming element content of the black spots on the three-point area on the surface of tableware ceramic

Unsur	Kandungan Unsur (% Massa)				Standar Deviasi
	Area 1	Area 2	Area 3	Rata-Rata	
C	4.83	0.00	2.89	2.57	2.431
O	34.27	39.97	32.21	35.48	4.020
Na	0.61	0.70	0.00	0.44	0.381
Mg	1.13	1.72	1.22	1.36	0.318
Al	7.17	8.44	5.47	7.03	1.490
Si	21.82	28.50	10.29	20.20	9.212
K	1.58	1.84	0.00	1.14	0.996
Ca	6.30	9.42	4.35	6.69	2.557
Fe	22.29	9.41	43.57	25.09	17.251

Testing is conduct by firing the x-ray to the three-point area with black spots, in the fired three point area appear elements forming black spots. In general, based on EDS test results there are nine elements forming the black spots on the ceramic tableware, with different presentage. These elements are carbon, oxygen, sodium, magnesium, aluminum, silicon, potassium, calcium, and iron elements with respective percentages presented in Table. Of the three point area black spots that have been tested EDS, there are the contents element also as a basic element forming the ceramic itself, such as silicon, oxygen, aluminum, potassium, and sodium, with a percentage that is not much different from each other from the three point area. Overall the biggest element of forming the black spots on the three-point area are the elements Fe and elements O, because the element O is the ceramic-forming element, therefor element O considered the must exist element of ceramic forming, so element Fe is the dominant element that causes the appearance of black spots, this is caused by the phase boiling point of iron is at temperature region 1535 ^{0}C. Ceramic burn temperature directly related to the maturity temperature, which is the state where pottery has reached maturity precisely without changing its form. To be turned into a ceramic clay, the clay has been molded to go through the process of burning at temperatures exceeding 600 ^{0}C. After passed these temperatures, the clay will transform into a solid, hard, and permanent mineral, which are called ceramics. Clay burned less than 600 ^{0}C yet have the proper maturity despite changes ceramics, Clay maturity temperature or vitrification is ceramic conditions that have reached right maturity temperature without changing its form. therefor before conduct the combustion process, need to know in advance the type of clay being used to form ceramics, clay maturation temperatures have a fairly wide range, which is between 600 ^{0}C - 2000 ^{0}C. If the clay is burned at low temperatures already crystalize, means vitrified clay is reached. From Fe boiling point temperature data and ceramic strength forming point, in Fe melting temperature phases, the Fe elements that have reached perfection melting during the vitrification process will traped and can not be compounded/melt with the formation of the ceramic in the process, thus leaving a black Fe melt point, because of the element carbon that were brought by Fe. The size of the Fe molten form depending on how many of the elements Fe trapped in the process of vitrification.

XRD Analysis Data Result

XRD diffraction pattern consists of several peaks in the plot on the y axis, and the diffraction angle measured in the plot on the x axis. Each peak or reflection in the diffraction patterns caused by the diffracted x-rays from the field in the XRD test specimen. Each peak has a distinct high intensity, the position of peaks that occur in the XRD test depends on its crystal structure. The XRD test results on samples of raw materials and biscuit ceramics are considered to allow the occurrence of black spots is known that the matrix phase Si O with compounds ceramic formed is cristobalit, trydimite, quarts, silicon oxide, and there is also an element of Fe incorporated in compounds Aluminum Iron Carbide (AlFe3C0.69). From the XRD results can be indicated that the Fe element in the form of Iron Carbide Aluminum compounds (AlFe3C0.69) hypothesized a major cause the formation of black spots on tableware ceramic. This confirmed with EDS test result, that stated in table 4.2, EDS test results showed that impurity element composition Fe has a high enough percentage figure reached 43.57% with other ceramic matrix composer elements like Si, O, Al.

H. Root Cause Analysis (*FTA*)

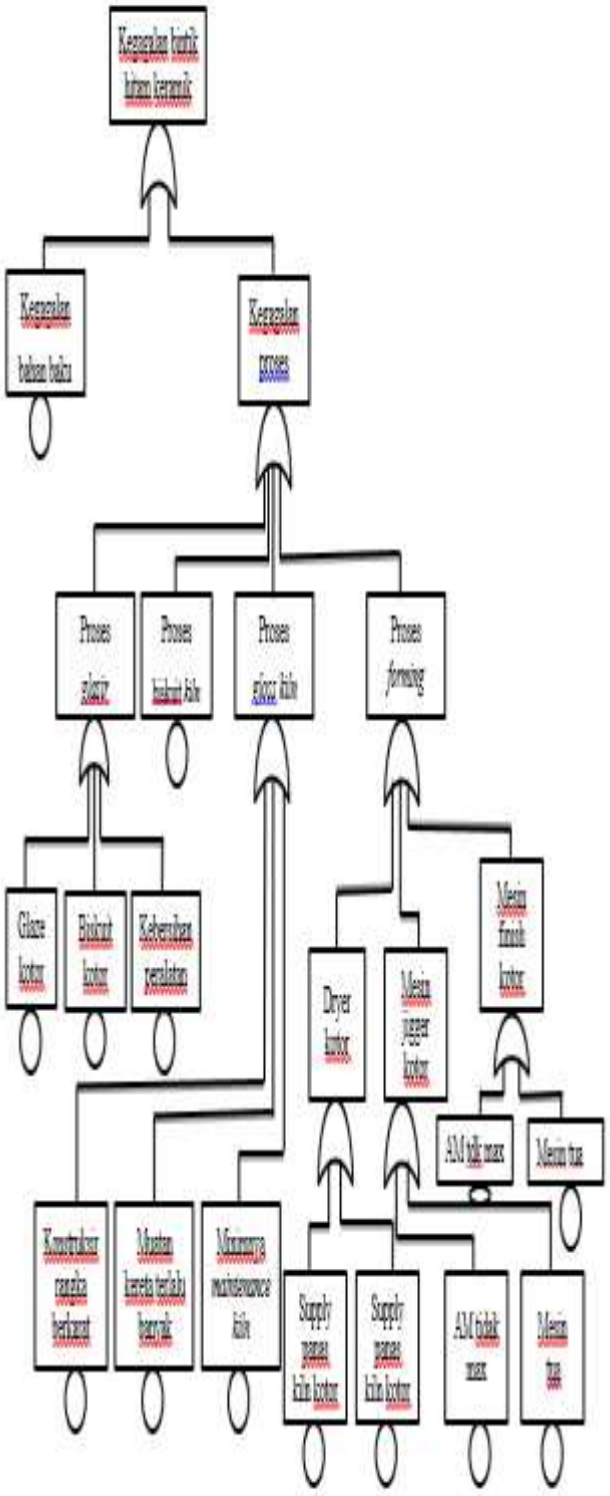

Fig 10, Black spot fault tree analysis

V. CONCLUSION

Based on the results of the discussion in this study, it can be concluded as follows :

1. The causes of black spots defect that occur on the surface of the ceramic tableware caused by factors of production process.
2. According SEM test results, found out that black spots occur because of the Fe element can not be decomposed in the combustion process.
3. The most contribution in appearance of black spot is the forming production process.
4. The production process of forming that causes black spots occur in the dirty dryer areas and jigger machine.
5. The main raw material is not indicated Fe containing compounds, but in the end result already found Fe compounds in their biscuits.
6. The more the content of Fe which forms black spots, the more intense the color of black spots.
7. The black spots are formed occures in the glaze layer.

Suggestion

1. In the future it is necessary to study to decrease or even possibly eliminate the Fe element in the production process start from material to the process.
2. Cleaning process in production facilities should be proceed periodically.
3. Need to do research on the possibility of the addition of certain substances to eliminate the black spots.

REFERENCE

[1] Ho Hwie Chie and Jamuar Nasution, "*Porcelain Product Quality Analysis*"Comtech Vol 6, 2017.

[2] Barry Carter & Grant Northon,"*Ceramic Material Science & Engineerin,*", 2016.

[3] Kirk Othmer, "*Encyclopedia of Chemical Technology*," Willey America, 2005.

[4] www.ceramic.org, "*Structure & Property of Ceramic*," Publish on Mayst, 2014.

[5] Minto Supeno, "*Bentonite Terpilar & Application*," USU Pres, Medan, 2009.

[6] Yvone Hutcinson, "*Ceramic Technology For Potters & Sculptor*," Philadelpia University America, 19966.

[7] WE Worrall, "*Clay & CeramicRaw Material* ," Elseiver Applied Scienc, New York, 1986.