Degradation of nonwoven polymer fabrics for bag filters with acid gases

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学位論文要旨

Polyphenylene sulfide (PPS) filter material has been commonly used for bag filters. In incinerating conditions, these bag-filter materials are exposed to high temperature and acid gases such as sulfur dioxide (SO_x), nitric oxide (NO), etc. Its durability to acid gases at high temperature is not far from complete understanding. Its degradation in the form of either N-atom-containing liquid (e.g., nitric acid) or gas (NO) has then become an interest of this study.

1. Degradation of semi-crystalline PPS bag-filter materials by NO and O_2 at high temperature

In incineration plants, nitric oxide (NO) and oxygen (O_2) are the two major gaseous components, which degrade the mechanical properties of the bag filter media. Based on the experimental results of mass, dimension, morphology, crystallinity, fiber diameter, fiber orientation, and fabric strength, the degradation (or change) in mechanical properties of polyphenylene sulfide (PPS) needled fabrics is related to two phenomena, i.e. the crystallization and the degradation of amorphous regions and partial crystalline regions. Both processes affect the fabric strength, competing with each other. The relation between strength and crystallinity is divided into three phases: (1) strength is dominated by crystallinity, (2) strength is dependent on both crystallinity and defects or damages in amorphous regions, and (3) strength and crystallinity decreases simultaneously due to the deterioration of amorphous regions and partial crystalline regions. An increase in NO has a

potential to increase the deterioration rates of amorphous and crystalline phases but the crystallization process is not affected. On the contrary, an increase in O_2 concentration leads to enhancement of both crystallization and deterioration.

2. Degradation of bag-filter non-woven fabrics by NO at high temperatures

Poly-phenylene sulfide (PPS) non-woven fabrics are often used at high temperatures, for bag filters in incinerating plants. Even though they degrade in the presence of acid gases, there has been not much information on the degradation of mechanical properties of PPS in nitric oxide (NO). At 200°C, which is generally the highest operational temperature of bag filters, PPS fabrics gradually lost its elongation even if the modulus is barely unaffected. On the other hand, at 250°C, which is near its melting temperature of 285°C, the modulus increases while the elongation decreases. Contradictorily to our first guess, PPS does not soften near its melting temperature, and becomes even more rigid. Our hypothesis then becomes that crosslinking and branching dominate around 250°C, leading to the embrittlement of PPS bag-filter materials and severe strength loss. Therefore, it is our recommendation that the operational temperature of PPS bag filters should always be below 200°C and the NO concentration should be far below 1000 ppm, at which chemical degradation occurs severely.

3. Mechanical degradation of filter polymer materials: polyphenylene sulfide

Polyphenylene sulfide (PPS) is known as a material resistant to high temperature and chemicals; however, there are arguments on the durability of PPS non-woven fabrics to chemicals, such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl). Therefore, this work aims at investigating the degradation of PPS non-woven fabrics in HNO_3, H_2SO_4 and HCl, and at confirming acid durability of PPS non-woven fabrics. In addition, this paper also studies the interaction among these three acids by measuring the retention of strength in binary or tertiary mixtures of these three acids. A discussion has been made on the acceleration/ retardation of PPS degradation by the interactive effects, and also chemistry related to the degradation by these acids.

Furthermore, there is a linear relationship between the nitric acid concentration and the proportion of carbon in the remaining PPS structures after 100 hours of acid exposure. Also, this proportion of carbon is a good indicator of the retained strength in PPS fabrics.

学位論文審査結果の要旨

平成18年8月3日に口頭発表と質疑応答を行い、その後に開催した学位論文審査会において以下のように決定した。

本論文は、都市ゴミ焼却炉などの排ガス処理に使用されるバグフィルタ用ろ材のうち、高分子Polyphenylene sulfide (PPS) 繊維からなる不織布について、高温での酸性ガスによる劣化を検討したものである。焼却炉排ガスを想定して、高温（200℃）で酸性ガス（NO）と酸素へPPSろ布を暴露して引っ張り試験を実施した。その結果、高温ではPPS繊維のアモルファス領域の劣化と結晶度の増加が併行して進行することを見いだし、ろ布の劣化機構を提案した。また、排ガス中の酸ミストへの暴露を想定し、酸溶液（塩酸、硝酸、硫酸）へPPSろ布を浸漬して引っ張り試験を実施し、硝酸に対してはPPS繊維が粒子化して脆化し、硝酸と他の酸が混在すると劣化が加速されることを明らかにした。そして、200℃、250℃において、NOによるPPSろ布の劣化を窒素雰囲気中と比較し、いずれの温度においてもNOが1000 ppm存在すると、強度はあまり変化しないが、繊維が硬化してろ布の伸びがほとんどなくなることを明らかにした。

以上のように、本論文は、高温におけるバグフィルタ用PPSろ布の酸による劣化に関し、劣化の機構を明らかにするとともに、劣化とPPSろ布の機械的強度との関係を与えており、実用的にもその価値は高く、博士（工学）の学位に値すると判断する。