SELF-ASSEMBLED NEEDLE-LIKE SPINEL COMPOSITES ON ALLOY SURFACE AS SPECULAR ABSORBER

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1. Introduction

Spectrally selective absorbers used in solar collector are known to improve efficiency of solar-thermal conversion. A desirable selective absorber is characterized by maximum absorption (α) over the solar spectrum (0.3 ~ 2.5 μm) and low thermal emittance (ε) at operating temperature(Salmi et al. 2000). This is realized by low reflectance of absorbing surface in the solar main irradiation spectrum (nearly zero) and high reflectance (close to one) in the IR region. For practical reason, a good selective coating features optical property of $\alpha > 0.9$ and $\varepsilon < 0.2$.

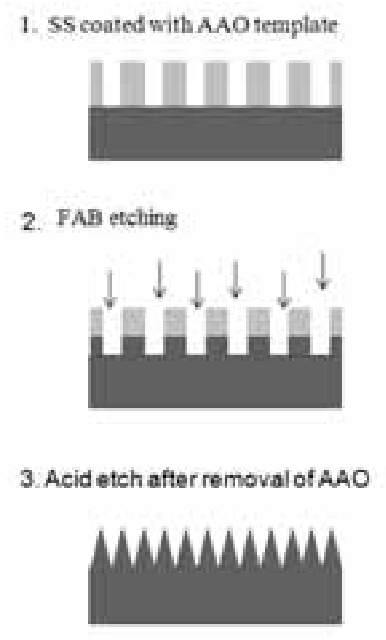
Of all types of selective absorbers, the surface texturing exhibits superior optical properties and thermal stability. Needle-like, dendrite, conic, or porous microstructure is constructed on a single-material surface called intrinsic materials, such as W, Mo, Si, etc. Rephaeli et al. (2008) have recently shown the wide angle absorption of tungsten pyramid structure as selective absorber through optical modeling. The textured surface on intrinsic materials is amazing because of its high absorption, stability at high temperature and convenient optimization through modeling. One problem concerning the textured surface is the difficulty of fabricating the desired structure as demonstrated (H Sai et al., 2001). Another is the limited absorption of a single material in the whole solar spectrum due to its intrinsic optical properties.

In this paper, we have presented a selective absorbing surface of spinel materials fabricated on metal alloy surface. The surface features organized conic geometry of nano-scale, efficient for light trap. Both the period and height could be justified to optimize the absorbing selectivity. Materials constructing the surface are composites of spinel ferri-, nickel oxides. Diffuse reflection of the film is measured on a Lambda 950 spectroscopy in 0.3 ~ 2.5 μm and FIRT in 2.5 ~ 25 μm. Both optical selective absorption properties and thermal stability at high temperature renders this selective surface superior candidate for receiver at mid-high temperatures.

2. Experimental work

2.1. Sample preparation

Stainless steel was used in fabricating the selective surface because of its chemical composition, such as Fe, Cr, Ni, etc, which are the transition elements widely used in selective absorber, and direct application in the high temperature solar thermal plant using SS tube to transit heat from the receive to electricity generator. The whole procedure is illustrated as scheme 1, firstly, SS coupon of 3cm*3cm, 0.3mm thick was masked with AAO template (the preparation of AAO is described by (Masuda and Fukuda 1995)); second, etching holes on the SS surface by applying FAB technique; at last, the SS coupon was place as working electrode; graphite plate was used as the counter electrode, the two electrode system was placed in a mixed chromic and sulphuric acid electrolyte. During electrochemical treatment, potential modulated as square wave was applied. The higher and lower potentials of square wave pulse was adjusted in order that absorber surface was formed. After the treatment, the surface has a black appearance, and then rinsed with stilled water, ready for characterization.



Scheme. 1 Fabrication process of the needle structured surface

2.2. Characterization

The optical measurements in the wavelength range 0.3 ~ 2.5 μm were made in a Perkin-Elmer λ950 double-beam spectrophotometer equipped with an integrating sphere. The total reflectance was measured relative to a $BaSO_4$ reference and the solar absorptance was calculated using ISO standard 9845-1, normal radiance, AM1.5.The infrared near normal specular reflectance was measured between 2.5 and 25 μm with a Bruker Equinox 55 double-beam spectrophotometer. An evaporated gold mirror was used as a reference. Thermal emittance was calculated from the reflectance measurements using a surface temperature of 100℃.

The surface morphology was characterized by Atomic Force Microscope(AFM) with a scanning range of 5 μm in tapping mode.

3. Results and Discussion

Fig.1 shows a scanning electron microscope (SEM) image of a porous alumina membrane mask. In this figure , the inter-pore distance, pore diameter and the thickness of the membrane are about 100nm, 80nm, and 300nm. The physical parameters can be adjusted through applied voltage and post widenning treament, inter-pore distance of 100-300nm, pore diameter of 60-150 could be achieved. These parameters determined to some extent the structure of the modified SS surface.

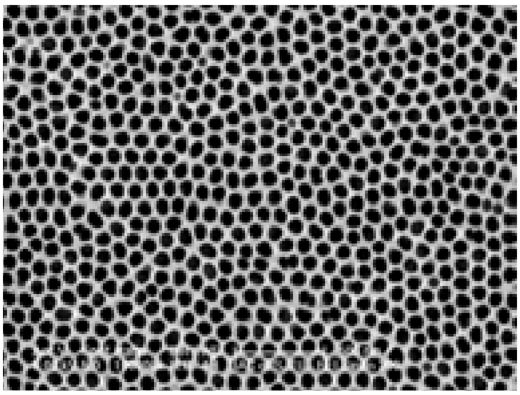


Fig .1 AAO template prepared through two-step anodization

Fig.2 shows an atomic force microscope (AFM) image (5μm*5μm) of the modified SS surface using a AAO mask with inter-pore distance of 150nm and pore diameter of 80nm. The surface presents as a needle-like forest, with an average height of 100nm and distance of neighbouring tips is about 100 nm. The surface features some extrodinary peaks that is 2 to 3 times highter than the main domain, which is caused by the uneven etching of the FAB process and the post acid treament.

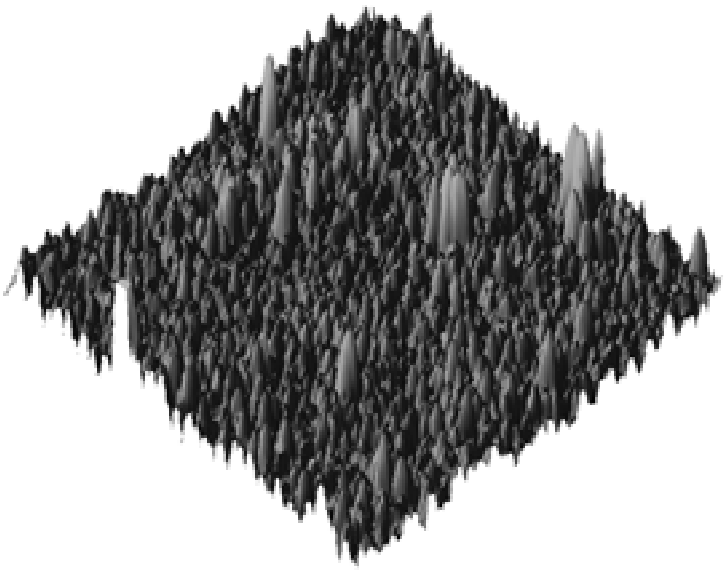


Fig .2 Surface geometry of the selective absorbing film

Surface texturing is a common way to obtain spectral selectivity by the optical trapping of solar energy. The emitance could be adjusted through microstructure modification. However, there is a trade-off between a highly absorbing coating and one with lower emittance. Highly absorbing coatings appear rough and porous. Coating with low emittance are smooth,dense, highly reflective, and mirror-like to thermal energy. In this work, since the absorbing layer was fromed directly on the SS surface, the absorbing feature was determined to a larger extent by the composition of SS elements, mainly, Cr, Fe, Ni. It leaves surface microstructure to adjust the emmitance and absorption. The microstructure is, in this case, specified as period of the needle-like compound and its height.

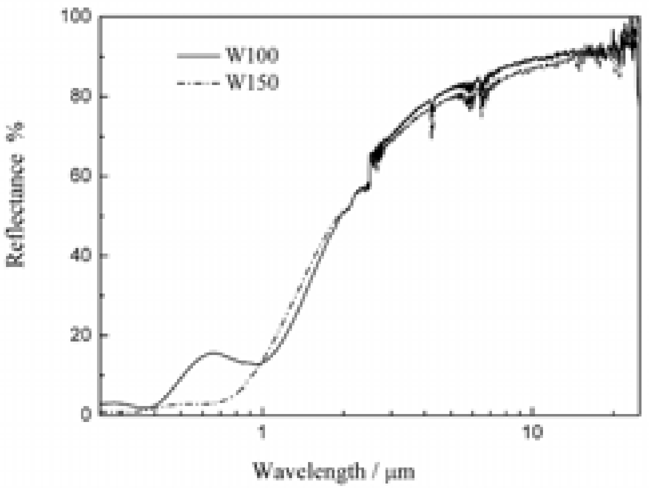


Fig .3 Reflectance of the selective surface with different period interval, 100nm period (full line) and 150nm period (dansh line)

Fig.3 presents reflecting curve of the modified SS surface with different period. Period is defined as the distance between two neighbour “needle”, surface with small period looks more dense while that with big period looks rough. Surface of 100 nm (W100) period behave quite different optical property comparing that of 150 nm (W150) in the visible and near infrared range. Reflectance of W100 is much higher than that of W150 from 0.4μm to 1μm, where located the the highest density of solar energy, resulted in the mass energy loss for the absorbing surface. Increasing period is a facile way to reduce surface reflectance and extend the absorption cutting-off to longer wavelength, however, larger period also leads to lower reflectance in the infrared region. As shown in Fig.3, comparing with W100, the reflectance of W150 is 2% lower, further increase of period will increase the emmitance accordingly.

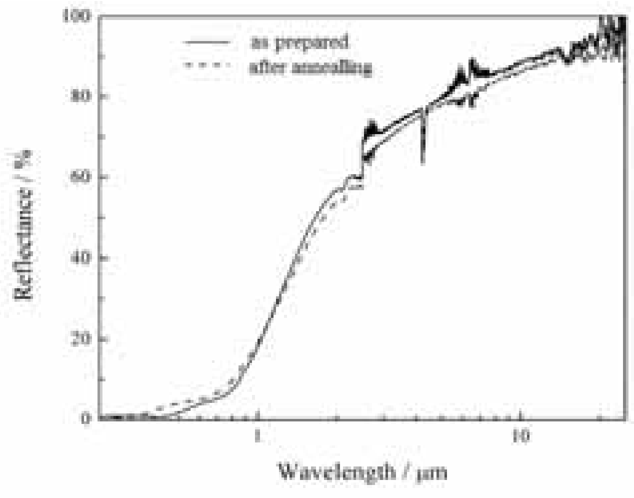


Fig .4 Reflectance comparison of the selective surface as prepared (full line) and after annealing (dash line).

Since the aim of this work is developing selective surface that is stable at high temperature, thermal stability and oxidation resistance test are necessary for this evaluation. The test is carried out in an oven at presence of air, the temperature is elevated to 200 ℃, 300 ℃, and 400 ℃. While the spectral reflectance barely change below 300 ℃, extraordinary break down happens for the absorber above 400 ℃, preliminary analysis shows that crystallization of the spinel composition is the main reason, details will be explained in other publication. Fig.4 is the reflectance comparison of sample as prepared and after annealing at 300 ℃ for 100 h, little difference was observed in the graph. The calculated absorptance and emmitance are $\alpha = 0.91$ and $\varepsilon = 0.08$ at 20 ℃, further optimization could improve the value of α to 0.95, while the emittance is also increased.

4. Conclusion

A needle-like textured surface was fabricated on the SS substrate. This structure is favorable for the light trap and anti-reflection. Considerable solar absorption was achieved, with α ranges from 0.91 to 0.95. the structure and composition was stable at high temperature up to 300 ℃, while optical properties were barely changed. Further investigation revealed that the optical break down resulted from the crystallization of composition at 400 ℃, which renders the possible use of this absorber at mid-high temperature.

5. References

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