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A new concept for solar energy thermal conversion

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A material has been developed which allows a new approach to be made to the conversion of solar energy to heat. It consists of a dense array of metal whiskers grown with spacings of a few wavelengths of visible light. The material selected has low emissivity, and achieves significant optical absorption by trapping the light by a geometric maze effect. We have deomonstrated that absorption of normal incidence light is greater than 98% from 0.5 to 40-μm wavelengths, and hemispherical emissivity at 550 °C can be made less than 0.26. Since surfaces can be made of a single refractory element, such as W, high-temperature solar conversion (550 °C) should be maintained with good surface stability.

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The conversion of incident solar light to thermal energy has recently received widespread interest.[1] Since Kirchoff's law relates absorptivity and emissivity, modern efforts in solar absorption attempt to obtain materials which have high absorptivity in the solar wavelengths (visible spectrum) and low emissivity at electrical power plant operating temperatures (near-infrared—typically 550 °C which has 50% Carnot efficiency in later conversion of heat to electricity).

The devices fabricated using this concept are multilayered structures called wavelength-selective absorber stacks. These devices have problems of stability at moderate temperatures (~550 °C), and demand submicron thickness tolerances over the wide areas necessary for solar conversion.[2] So little is known about thin-film interaction and diffusion that film stability has been the major obstacle in the operation of these devices.[2]

We propose a new approach to the problem: We suggest that rather than absorb solar light directly using intrinsically highly absorptive (in the solar wavelengths) materials for the surface, a microstructure similar in geometry to an acoustic anechoic surface be used. The surface would consist of a dense forest of aligned needles whose diameters are of the order of visible wavelengths; the spacing between needles is several wavelengths. This surface would absorb with high efficiency because of multiple reflections as the incident photons penetrate the needle maze (this is similar to the acoustic absorption by anechoic walls). Since absorption is dominated by geometric factors, the surface of the structure can be made of a material which emits poorly in the infrared (blackbody temperature of 550 °C). We hypothesize that such a material would have an absorptivity of unity for most wavelengths smaller than the needle spacing over a narrow incident cone about the needle direction. However, this high absorption cone, which will have high emissivity, will not greatly affect the total hemispherical emissivity because of its small solid angle. If the surface is made of a metal with low emissivity, the total hemispherical emissivity may not significantly increase above the normal emissivity of the metal. We have fabricated such an absorber using tungsten single-crystal whiskers (or dendrites) grown on a variety of substrates.

The process used was the hydrogen reduction of tungsten hexafluoride (WF_6) at atmospheric pressure. The apparatus used is described elsewhere.[3,4] Various substrates were used with equal success: sapphire, polished tungsten, and stainless steel (No. 306). The cleaned substrates were placed on a graphite susceptor, and the system was initially purged with hydrogen. The substrates were heated to between 450 and 500 °C. WF_6 and H_2 flow settings were adjusted while in a by-pass

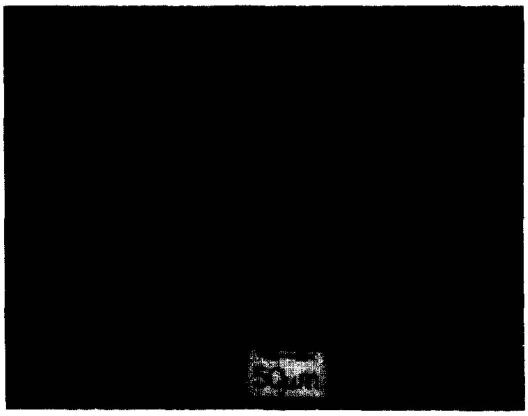

FIG. 1. Typical tungsten surface which has over 98% absorption of normally incident photons in the wavelength range 0.4—40 μm. Only the larger dendritic array is seen, with the largest dendrites being about 80 μm high. Below this is a denser forest of 5-μm-high dendrites. This sample has a hemispherical emissivity of 0.28.

mode, and then directed into the reactor where W was deposited on the substrates. The hydrogen flow rate was about 10 liters/min with a WF_6 flow of 0.1 liters/min. The film thicknesses ranged from 125 to 500 μm. The structure of the films deposited on sapphire was analyzed[5,6] and it was found that the $(11\underline{1})$ W $\parallel$ (0001) α-Al_2O_3, and in the plane [110] W $\parallel$ $[11\bar{2}0]$ α-Al_2O_3. The orientation is twinned in two specific ways; one showing sixfold symmetry, and the other with threefold symmetry. The orientation of tungsten deposited on polished tungsten and stainless steel was also highly preferred; the fiber texture was twinned with (111) planes parallel to the surface of the substrate. With each type of substrate and with the conditions described, the growth was dendritic and showed a stalagmitelike structure, as shown in Fig. 1.

The deposition showed, typically, a three-layered growth. The tungsten next to the substrate was continuous and polycrystalline, with a high degree of texture. The dentrites were basically of two sizes. The smaller forest averaged 10 μm high with a spacing of about 5 μm. The larger dendrites were 40—60 μm tall, with a spacing of 40—60 μm. A typical cross section is shown in Fig. 2. This double dendrite structure may be responsible for the very large wavelength range of absorption.

The growth of the dendrites on the three substrate materials was similar, except that the W film when removed from the sapphire disks produced self-supporting films which were mirror smooth on the side which contacted the sapphire substrate.[6]

We believe that the important point was that the arrays were formed from the fabrication technique, and can be formed on any material onto which tungsten adheres. The growth on the stainless steel simulated direct deposition on common structural high-temperature material (boiler tubes). The surfaces were tested in absorptivity on two standard infrared reflectance spectrometers for incident wavelengths from 0.5 to 40 μm. For normally incident light, the tungsten dendrite structure measured less than 2% normal reflectance for the entire wavelength range of the instruments. An independent measurement of *total* hemispherical reflectance was made for the primary solar wavelengths, and less than 4% of the normally incident light was found to be reflected.

Hemispherical emissivity was measured two ways: In one technique, 2-cm square disks were covered with dendrites, heated in vacuum to 650 °C, and then dropped into a cold blackbody cavity. Fine thermocouple wires suspended the disk, and the time was measured for the temperature to drop from 575 to 525 °C. Similar measurements were made with identical disks coated with shiny Au and W, and with iron black, as consistency checks. Typical emissivities for the dendrite samples were in the range of 0.26—0.30.

Another measure of emissivity was made by suspending dendrite-coated disks in cold blackbody cavities, and measuring the electrical power necessary to sustain a temperature of 550 °C. The emissivity measured agreed with the values obtained using the first technique.

We attempted to decrease the emissivity of the samples by coating the dendrites with Au (emissivity of 0.02 versus 0.08 for W). Samples were coated by dc sputtering about 1200 Å of Au which covered the sides as well as the tops of the dendrites. The emissivity dropped by about 20%, but the absorptivity also dropped from 0.98 to 0.86. This result indicates that the Au overcoating process may be beneficial, but that attention must be paid to optimizing absorptivity.

In order to determine the effects of varying dendrite width, samples were etched in $H_2O_2 + NH_4OH$. The dendrites preferentially etched from the sides and became much narrower. No effects could be seen in absorptivity or emissivity of these samples; however, the technique may allow fine adjustment of the absorption characteristics of the surface.

We found that the hemispherical emissivity of the dendrite surface could be estimated by measuring the angle of tilt from normal incidence where the surface appearance changes from black to metallic. The change is rather abrupt. The surface emissivity, assuming azimuthal symmetry, can be given by

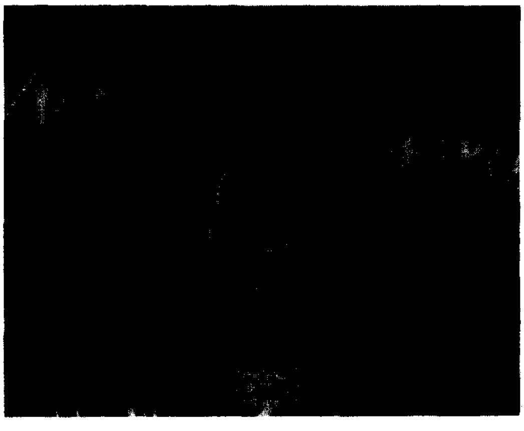

FIG. 2. Cross-section view of a tungsten sample showing the smaller dendrites. The photons average over 50 reflections before being absorbed.

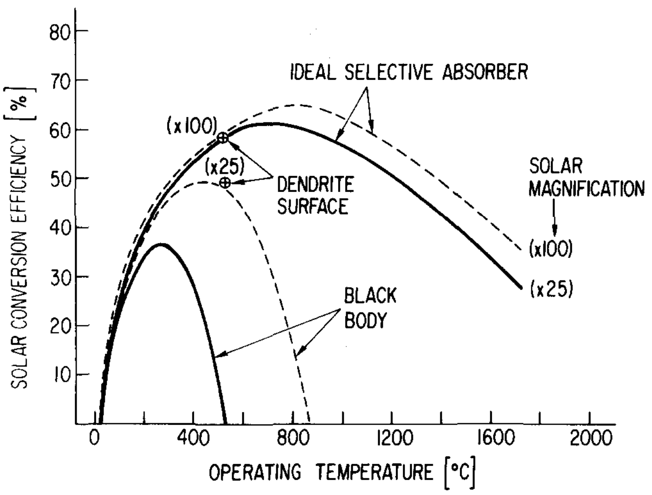

FIG. 3. Efficiency of conversion to work plotted for various absorbers assuming solar magnification of 25× (solid lines) and 100× (dashed lines). The plots include both absorption efficiency and a Carnot efficiency for conversion to useful work. The upper two curves are for theoretically ideal selective absorbers (as described in Ref. 7). The lower two curves are for blackbodies. Also shown at 550 °C are two points for the experimental dendrite surfaces. For moderate magnification (25×) the dendrite surface has an efficiency close to that of an ideal selective absorber. For very high magnification all three surfaces become efficient. A basic economic problem of solar conversion is the trade-off between precision mirror guidance systems (magnification) and high-efficiency absorbers.

$$\epsilon_H = (1/2\pi)\int \epsilon(\theta)\cos\theta\, d\theta, \qquad (1)$$

where ϵ_H is the hemispherical emissivity, and $\epsilon(\theta)$ is the specific emissivity into polar coordinate angle θ. The integral is evaluated over the hemisphere. If we simplify the geometric effects so that for solid angle Ω about normal incidence the dendrite surface has total absorption and unit emissivity, and beyond that angle the surface has zero emissivity, we may explicitly solve Eq. (1) to obtain

$$\epsilon_H = \sin^2\theta_\Omega, \qquad (2)$$

where θ_Ω is the half-angle of the cone of total absorption. For actual dendrite surfaces, we find that for the tilt angle of the surface to a grey area of 50% reflectance, θ_Ω is a reasonably accurate estimate of hemispherical emissivity using Eq. (2).

With the absorptivity and emissivity of the tested samples, we may compare this type of solar absorber to conventional selective-wavelength absorbers. Keyes[7] has discussed in detail the characteristics of an "ideal" absorber which has total absorptivity in the primary solar wavelengths, and zero emission in the infrared. This absorber is not perfect, for a small amount of the solar spectrum is in the infrared and this is not absorbed, and part of the thermal radiation of the absorber overlaps the solar spectrum and is emitted. The thermal conversion efficiency can be combined with a Carnot efficiency to estimate ideal conversion to work. The keyes approach is used in Fig. 3 to plot conversion of solar energy to work as a function of absorber operating temperature and solar magnification. The total efficiency is small at low temperatures because of poor Carnot efficiency. At high temperatures the efficiency drops because a large overlap occurs in the solar spectrum and the absorber's radiation wavelengths.

Also plotted in Fig. 3 are efficiencies from ideal blackbodies which absorb and emit at all wavelengths. At high magnification there is not much difference between a blackbody and ideal absorbers. This is because at each temperature radiative emission is a constant from a given surface, and as more heat is made incident through increased magnification, *any* absorber efficiency increases. However, large-scale magnification above 20–50× is not considered practical using modest mirror drive mechanisms and because of atmospheric aberration and windage effects on the mirrors.

We include in Fig. 3 two evaluations of the dendrite surface conversion efficiencies at 550 °C. We cannot plot this surface as a function of temperature as we have not yet done extensive measurements of its spectral characteristics at other temperatures.

One can see in Fig. 3 a basic trade-off in solar conversion economics. If one puts considerable effort into obtaining high magnification (say 100×), then one can use a blackbody absorber without much degradation at typical operating temperatures. If one uses a mirror system of modest magnification (say 25×), then considerable effort must be taken on obtaining a high-efficiency absorber.

In conclusion, we have demonstrated a new approach to solar energy conversion. The dendritic array we have fabricated absorbs normally incident light efficiently because of multiple reflections of the incident photons. The surface is made of a low-emissivity material which reduces radiative losses. Since we use a refractory single element surface, there are no stability problems as associated with conventional selective absorber surfaces. We have demonstrated the fabrication of the dendrites directly on structural stainless steel.

We wish to thank A.H. Nethercot for suggesting Fig. 3. We understand that studies similar to those of this paper are being conducted by R.B. Kaplan[8] using rhenium dendrites.

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