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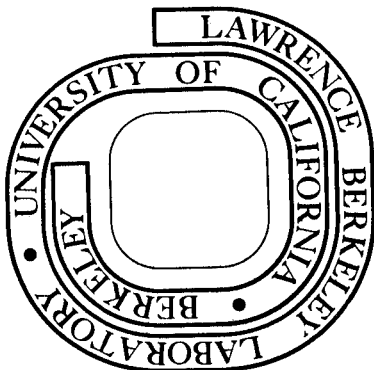
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COATINGS FOR ENHANCED PHOTOTHERMAL ENERGY COLLECTION I
Selective Absorbers ital

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ABSTRACT

For economical and efficient utilization of solar energy various types of absorber coatings and preparations can be used for solar collectors. In this study several varieties of commercial and research selective absorbers are reviewed and tabulated for application. For many of these coatings, detailed reflectance, emittance, and thermal stability data are presented. Selective coatings can take advantage of various optical absorption methods including light trapping, particulate coatings, semiconductor-metallic layers, multilayer films, quantum size effects and also intrinsic absorption. The results of this study revealed many promising low temperature (150°C-300°C) absorber coatings along with a few highly engineered coatings which can withstand temperatures above 500°C.

1. INTRODUCTION

If we are to utilize solar energy for specific purposes or end uses we need to know the role coatings can play especially when they are a crucial and important consideration in terms of energy collection and cost effectiveness. Also, we should know how various coatings perform, the types available, projected cost and potential areas of application. Then it is important to point out problems associated with usage of particular coatings.

The following study is aimed at the technical reader who is concerned about the properties of selective absorber coatings for the collection of solar thermal energy. The scope of this report is to put forth data about commercially available or potentially available absorber surface coatings and to study them in the context of their potential usefulness, inherent limitations and applications to various end use temperatures.

It is important to review briefly the current applications of coatings. Selective surface coatings play an important role when temperatures are required in the vicinity of boiling water because radiative losses become large at these temperatures. At higher steam temperatures, evacuated tubes and selective absorbers are used to cut down on increasing convective and radiative losses; usually, these collectors are of the concentrating design.

Many of the various selective surfaces can be applied to a variety of materials. Common absorber plate materials are steel, copper and aluminum and to a lesser degree, glass and stainless steel have been employed.

After a brief outline of optical measurements, the following sections will reveal details about the usage of various materials and the combination of their physical properties to obtain useful absorber coatings.

2. OPTICAL MEASUREMENTS

In most cases reported, for selective coatings, reflectance measurements are used to derive both absorptance (a_w) and emittance (e_w) of the various materials. In practice, both absorptance and emittance are integrated values, however, emissometers are employed to measure emittance. Some investigators use direct beam spectral reflectance measurements to characterize their samples, while others use hemispherical spectral reflectance and calorimetric methods. On the other hand, many do not even report the techniques used to obtain their values. As a result, discrepancies due to equipment and techniques are common and absolute values for any one particular surface are not well defined.

3. SOLAR SELECTIVE ABSORBERS

In general, a selective absorber, sometimes called a selective surface, is a material or coating which exhibits optical selectivity; that is, optical properties which vary greatly from one spectral region to another. In the field of solar energy a selective absorber efficiently captures solar energy in the high intensity visible and the near infrared spectral regions while exhibiting poor infrared radiating properties. Accordingly, a selective coating will absorb and retain a high amount of energy from the sun while a non-selective surface, such as an ordinary black paint, will lose much of its absorbed energy by reradiation. For optimum efficiency the solar absorber should possess the maximum possible absorptance in the solar spectrum while maintaining a minimum infrared emittance. An example of this effect is shown in Fig. 1. The blackbody spectra shown in this figure represents the ideal distribution of energies radiated by the selective absorber operating at a specific temperature. Also, in this figure the wavelength distribution of the solar air mass 1 spectrum is shown for comparison.

Solar selectivity can be obtained by a variety of methods. These techniques are outlined in the following tabulation:

1. Intrinsic solar selective materials.
2. Optical trapping by surface cavities or physical wavelength discrimination.
3. Particulate coatings, composite film
4. Absorbing semiconductor/reflecting metal tandem.
5. Multilayer thin films.
6. Quantum size effects.

Many actual selective coatings consist of combinations of these groups. For example, a surface may exhibit both particulate scattering and semiconductor/metal tandem properties. In the sections to follow, these basic methods in obtaining selectivity will be discussed and exemplified by selected current research and commercial processes. A summary table (Table 2) will be presented at the end of this section for comparison of the various absorber types.

3.1. Intrinsic Absorbers

There is no intrinsic material occurring in nature which exhibits ideal solar selectivity. There are, however, materials that approximate the required solar selective characteristics, as shown in Figures 3 and 4. By study of these unusual materials it may be possible with the knowledge obtained to synthesize new or improved intrinsic selective absorbers. To reach this goal it is necessary to understand complex electronic structure and its influence on optical properties. If such an understanding is obtained then it would be possible to design absorbers outright by using solid state physics.

Two categories of materials are good candidates for intrinsic absorbers because they already exhibit at least one desirable absorber characteristic. They are transition metals and semiconductors. For each one to serve as an intrinsic absorber would mean that it would have to be greatly modified. In general metals exhibit a plasma edge (See Fig. 2) too early in the solar spectrum to be good absorbers. By creation of internal scattering centers it is possible to shift this plasma frequency towards the infrared. An example is MoO₃ doped Mo developed by Seraphin and Associates [1], as shown in Fig. 3.

Pure tungsten is shown for comparison; it is one of the most wavelength selective metals. By making a semiconductor highly degenerate it may be possible to suppress its plasma frequency in the infrared, making it a poor emitter then. Unfortunately, these adjustments to atomic structure are not as simple as portrayed; there are many subtleties and unknowns involved. Further considerations of these details and conjectures are discussed by Seraphin [1-3] and Ehrenreich [4]. In the following discussion unusual materials will be looked at, as they possibly may provide insights into the creation of truly intrinsic absorbers, not to mention advancement of the field of solid state theory applied to optical materials design.

Three transition oxides clearly indicating selectivity are shown in Fig. 4. All of these oxides exhibit optical transitions too early in the energy spectra, as depicted by the bracketed visible region. If, by some materials science means these spectra could be shifted to longer wavelengths, an ideal selective absorber might be created. The distinct feature of these oxides, as noted by Ehrenreich et al. [4], is an incompletely filled d-shell of the metallic ion. When this ion is combined with oxygen, these electrons become localized, resulting in this optical property. Also under speculation by Seraphin [3] is the addition of sodium to tungsten trioxide, WO_3 , resulting in a metallic oxide like ReO_3 . Another material is lanthanum hexaboride (LaB_6), a transmitting selective material exhibiting 85% transmission in the visible and 90% reflectance in the infrared. This material might have a heat mirror application if it were overcoated with a dielectric layer which would cut down the visible reflectance. To further develop

these intrinsic absorbers one must investigate the band structure of these various materials and others related to them. It is also necessary to understand the materials science of these compounds and its effect upon the resulting optical properties. Another important consideration is to determine the influence of structural imperfections, such as dislocations, vacancies and interstitials, upon the optical properties of these materials.

3.2. Optical Trapping

A common technique used to obtain optical trapping of energy or wavelength discrimination is surface roughening. It is possible to produce a surface which would appear rough and absorbing to visible energy while appearing mirror like and poorly emitting in the infrared. An important point to note here is that the unroughened material would not have to exhibit a high intrinsic absorption coefficient in the visible region and because of this, metals roughened by some technique might make excellent optical trapping solar absorbers. Nearly ideal surfaces have been produced by chemical vapor deposition (CVD). The CVD deposition of rhenium by Seraphin [7] and tungsten by Cuomo et al. [8] results in a dendritic structure. These dendrites appear as conical needles or whiskers. The dendrite forests absorb high energy solar radiation by the geometry of multiple absorption and reflection as depicted in Fig. 5. The sum of these absorptions are very high with respect to the incoming radiation, although a single absorption might be quite low. In the thermal infrared region the wavelengths of energy are much larger than the dendrite spacings; the surface appears fairly smooth, acting like a poor radiator of energy.

The tungsten dendrite structure is made up of three distinct regions. The base is a continuous polycrystalline layer exhibiting a high degree of texture. On top of this layer are two different sizes of dendrites. This dual forest probably is responsible for the wide range of optical absorption, anomalous to a broad band absorption filter. Pettit et al. [9], found that anodization can improve the optical selectivity of the tungsten surface. A potential advantage with the dendrite absorber is that it can be used at an elevated temperature for highly concentrating collectors or high temperature steam generators. Most types of selective surfaces cannot withstand high temperatures greater than 350°C.

A fairly random dendrite coating can be formed directly on collector plates by reacting laminated metal layers in an exothermic atmosphere; as done by Santala and Sabol [10]. The most successful of this type of intermetallic absorber is the aluminum-nickel surface which consists of visible wavelength size cavities as depicted in Fig. 6. In general, optical trapping surfaces are in the developmental stage so many pertinent properties of the materials and techniques are unknown for immediate solar collector application. Various optical trapping surfaces are listed in Table 1 along with their solar properties.

Reducing the size of surface roughening to the order of the wavelength of energy desired to be absorbed, can increase the net absorptance of the absorber, but it can at the same time increase the infrared emittance. The amount of increased emittance is related to the micro-roughness and crystallite size. The net effects of micro-roughness can be quite complex for a realistic absorber. At very

fine surface roughness there is a trade-off between what is known as reflective scattering, due to cavities, and that of resonant scattering which is dependent upon the material and its morphology in the sub-wavelength size range. In the following section on particulate absorbers the details of resonant scattering will be discussed at length.

3.3. Particulate Coatings

There are two different mechanisms of absorption for particulate coatings, reflective and resonant scattering. Reflective scattering is obtained purely by the geometry of imbedded surface particles. These particulate surfaces appear to be wavelength selective by purely geometric multiple reflection means. Resonant scattering, on the other hand, deals with both the size and optical properties of the particles and surrounding media. The Mie effect and Maxwell-Garnet theory describe resonant scattering in an idealized way. These theories predict high forward scattering from particles much less than 0.10 of the wavelength of the incident energy. Actually, both theories are inadequate in describing real systems of particulate selective absorbers which consist of complicated dispersions of metallic or semiconductor particles in dielectric or conductive matrices. Suspension of metals such as chromium, copper, calcium and titanium can exhibit broad visible region resonance or absorption while appearing highly reflective or transparent in the infrared wavelengths. The exact frequencies of reflectance transition and absorption are controlled by the size, shape, distribution, and individual optical properties of the media involved. Characterization of a real system such as the quite promising

electroplated black chrome surface is difficult, because it is hard to identify and control chromium particle size and shape and the exact matrix composition of an amorphous oxide phase (Cr_2O_3), investigated by Lampert [11]. Shown in Fig. 7 is an electron micrograph depicting small particles of chromium in the size range of 150\AA imbedded in a chromium oxide host matrix. Also, this real surface shows reflective scattering by its surface, as seen in Fig. 8. Other investigators such as Driver [12] and Pettit [13], have noticed this effect in similar types of black chrome. The effect of substrate roughness and reflectance upon the properties of black chrome have been investigated also by Hogg and Smith [14]. This coating has been modeled by physical scattering theories by both Granqvist and Hunderi [15] and Ignatiev, et al. [16], although this coating appears to be much more complex than these models can easily describe. Reflectance values for various types of this successful coating are presented in Fig. 9. In this figure four types of electroplated black chrome are shown along with a cermet, made by Fan and Sprua [17], consisting of 29% chromium particles in a Cr_2O_3 matrix with crystallite sizes of the order 150\AA . The cermet surface attempts to model the more complicated black chrome surface and shows that RF sputtering can yield a very selective chromium black. By changing the thickness of the black chrome surface the optical transition can be adjusted as noted by McDonald [20,21] and Lampert [22]. The black chrome surface in many ways appears as a simple tandem absorber; the infrared spectral response does depend upon the properties of the base metal. Tandem absorbers will be discussed in the following section.

Other particulate surfaces, made by Williams et al. [23], can consist of very fine semiconducting particles such as PbS imbedded in a silicon paint, brushed onto a metallic collector surface. These finely divided particles give a high degree of forward scattering to accomplish absorption as shown in Fig. 10. Tin particles, 400Å size, suspended in a MgF₂ matrix represent another successful system, made by Zeller and Kuse [24], which exhibits high visible opacity and infrared transparency. Shown in Fig. 10 are various types of particulate absorber films depicting optical transitions either in the infrared or of visible wavelength regions. The silicon powder absorber coating investigated by Warren [25] represents a novel method of producing a semiconductor metal tandem. However, the nature of surface scattering remains as a very important consideration when such systems are employed as solar absorbers.

One hope in the utilization of the particle scattering phenomena for solar energy collection is by use of very fine particle sizes. If a paint consisting of very fine pigment particles could be made to satisfy the requirements for the Maxwell-Garnett Theory, then a painted metal might make a good selective absorber. This technique has already been attempted with some success by Moore et al. [26].

3.4. Semiconductor/Metal Tandems

If a metal is overlaid with a semiconductor then the semiconductor will absorb high energy solar radiation, while in the infrared wavelengths the tandem will act like a poorly emitting metal. The metallic like character of the tandem is due to the high transparency of the

semiconductor in this region. A schematic cross section of a tandem absorber is shown in Fig. 11.

One of the simplest single layer absorbers is an oxidized metal, where the oxide provides the necessary solar absorptance. Figure 12 shows representative materials. Such natural oxides appear very promising, if they can be stabilized and made to exhibit similar mechanical properties seen in the substrate. With temperature cycling, oxides can crack or spall, which may be a major drawback to their usefulness. Recently a technique has been perfected to color stainless steel by hot acid dipping. As a result, a complex oxide coating is formed and can be used as a tandem absorber (see Fig. 13). This technique has been analyzed by Karlsson and Ribbing [29]. They found that if this coating was to be used above 200°C it would require a passivating layer.

There are numerous semiconductor-metal combinations; a number of successful types are shown in Fig. 13. The oldest and possibly the easiest to make is CuO on Al; it was formed by spraying a solution of CuO on the metal plate and heating to make the final absorber. The other copper oxide surface noted in this figure is formed by a chemical conversion process much like methods to be discussed later. The lead sulfide coating was vacuum evaporated over aluminum. This PbS coating shows an interesting contrast to that of the PbS dendrite particulate coatings. Cobalt oxide is known refractory oxide and recent work has applied this coating to solar absorbers, by electrodeposition, oxidizing and doping procedures.

Another interesting tandem absorber is that of In_2O_3 on silicon investigated by Goldner and Haskal [35]. This coating combination works in reverse of the regular tandem coating. The top layer reflects the infrared wavelengths while the bottom silicon layer absorbs the high energy visible light. In the visible range In_2O_3 appears transparent, as may be seen in the section on heat mirrors. The reflectance for this unusual absorber is shown in Fig. 13.

A well refined tandem absorber is the University of Arizona's silicon absorber, produced by Seraphin and co-workers [3]. It consists of a silver reflection film covered by a diffusion barrier (anti-agglomeration layer), in turn covered with a silicon absorber. To reduce the high reflectivity of the silicon layer an antireflection layer is used. This may seem to be an over designed absorber but it is one of very few surface coatings which can withstand continuous temperatures in excess of 500°C with good stability. The reflectance of this high temperature absorber is shown in Fig. 14.

Tandem absorbers can be made from crystalline or amorphous materials in the form of powders or continuous films. Sometimes the presence of grain boundaries, imperfections or lack of atomic order can be beneficial in deriving the desired absorber characteristics. These absorber layers can be formed by various electrochemical, reactive and depositive means. It is because of all these factors that the tandem absorber is one of the most popular absorber designs.

3.5. Multilayer Thin Films

Multilayer thin films known as interference stacks are dielectric, metal combinations which act like a selective filter for energy absorption.

The desired effect of an interference stack is to trap energy between semi-transparent metal, dielectric and metal alternations. Particular wavelengths of solar energy are absorbed by multiple reflection in the dielectric-metal layers. Other wavelengths not corresponding to the absorption frequency of these layers are reflected. In general the dielectric need not exhibit intrinsic absorption in the visible energies. The thin metal layer usually is only $\sim 50\text{\AA}$ thick, to appear semi-transparent to incoming radiation. Being such a thin layer the actual composition is not well defined. Most of the incoming energy is believed to be attenuated in this metal layer. Quantum size effects, to be discussed later, may help describe the actual process of absorption response. Most multilayer films are produced by vacuum deposition or chemical vapor deposition.

An example of a variation of the standard interference stack is electrodeposited black nickel; two types are shown in Fig. 15. The Tabor coating exhibits the classic double minimum for interference films, shown around 0.4 and 1.0 micron wavelength. This coating consists of two layers ZnS and NiS brought about by a simple change in plating current density during electrodeposition. Honeywell has improved this process to give the upper curve in Fig. 15. Also by heat treating the coating, drastic shifts in the optical transition wavelength can be made.

Other examples of multilayer coatings are shown in Figs. 16. The Helio 09 absorber reported by Meinel, et al. [39] exhibits a rapid rise in reflectance, but a bit too early in the spectrum to be a good absorber. A better response is obtained from the Al-SiO₂ and Helio 96

coating which has a steep transition with good absorption. Another coating in Fig. 16 is the high temperature AMA coating ($\text{Al}_2\text{O}_3\text{-Mo-Al}_2\text{O}_3$) developed for space use by Honeywell, investigated by Peterson and Ramsey [40]. This coating can withstand temperatures in excess of 800°C while exhibiting good stability.

The disadvantage with most multilayer coatings is that they are fairly expensive to fabricate. Also, they can suffer from corrosion and interdiffusion at elevated temperatures. Each of these conditions result in degradation of the optical properties. Some coatings are sensitive to abrasion. The AMA absorber, on the other hand, appears not to suffer from many of these drawbacks. Some manufacturers of optical coatings claim that by use of automatic equipment and with high volume production, these vacuum deposited absorbers might be inexpensive.

3.6. Quantum Size Effects (QSE)

Quantum size effects occur in ultrathin films. These effects can result in the high absorption of visible light while maintaining a low infrared emittance. The critical thickness for the quantum size effect to be utilized in a metal must be nearly the size $20\text{-}30\text{\AA}$ and for a degenerate semiconductor, $100\text{-}500\text{\AA}$ is necessary. The combination of a QSE material and a metallic substrate can make a selective absorber. This effect has been observed in vacuum deposited indium antimonide (InSb) on silver and aluminum substrates. The absorption coefficient was measured for this film and the results are depicted in Fig. 17 for various film thicknesses analyzed by Mancini and co-workers (see Ref. [42]). Similar results should be observed in

semiconductors exhibiting sharp conduction band minima. This would require a low value of the ratio of electron effective mass to that of its free mass in the thin film.

The QSE may play an important role in multilayer selective absorbers. Frequently, thin metallic layers are used between dielectric layers. These layers are responsible for high solar energy absorption; QSE may help explain phenomena.

The major drawback in utilizing this effect in a realistic solar absorber is the stability and continuity of composition of the coating upon cyclic heating and atmospheric exposure. To understand and utilize the quantum size effect, further work must be performed on various semiconductors and metals.

4. APPLICATIONS OF COATINGS

By the use of the various coatings discussed previously certain solar energy collection efficiencies can be obtained. The decision to use or not to use a coating is usually an economic one. Since the economic issue is hard to address, due to a constantly changing industry, the following discussion will only cover gains in efficiency by the usage of a particular surface coating.

Two cases will be treated: a standard double glazed flat plate collector operating at 93°C (200°F) with 21°C (70°F) ambient, and a parabolic collector operating at 315°C (600°F) with the same ambient temperature. These collectors will operate at these fixed temperature requirements while the efficiency is allowed to change due to only an addition of a selective coating. In each case the assumption is made that sufficient amount of incident solar energy is available to maintain the end-use temperature. So in this way losses can be directly interpreted as declines in efficiency.

A flat plate collector is depicted in Fig. 18. The effects of using a selective absorber and a non-selective coating are shown in terms of comparative collection efficiency. Another application for these coatings is demonstrated by the parabolic trough concentrating collector (Fig. 19).

As a result it is obvious that at higher operating temperatures a selective surface becomes a very important consideration. Increases in net efficiency can range from 12-22% for a parabolic collector. Collection efficiencies as high as 45.6% and 62.5% can be achieved with the use of selective absorbers for these model collectors. Whether

a particular coating should be used or not would depend heavily upon the economics of the various alternatives, that is, in some cases all coatings may be cost effective and in other cases, few at all would be cost effective.

5. CONCLUSIONS AND RECOMMENDATIONS

As a result of this study the following general conclusions and recommendations appear to be valid for the use of coatings for enhanced photothermal energy collection.

1. There are many promising cost effective coatings for usage in solar energy. A few for low temperature use (150°C-300°C) are copper oxide chemical conversion, black paints, black nickel and black chrome, which appears to be the most stable. These coatings are favored because the capital equipment already exists and several of the processes have been used for years, although not for solar energy. For higher temperatures (300°C to 500°C and beyond), the multilayer AMA coating, U. of Arizona silicon absorber, tungsten dendrites, plasma sprays, and refractory paints appear to be good absorber candidates. Also, there appears to be a gap between the temperature application range 350°C to 500°C. Most selective absorbers operate up to 350°C or perform beyond 500°C; very few exhibit a temperature stability limit around 400°C, which would be adequate for most applications. There are still a multitude of coatings and processes which are promising, but not enough research has been performed to characterize them adequately.

Even though many promising coatings exist, very little is yet known about their operation and possible degradation in real operating environments. It is expected that the presence of moisture, heat, and atmospheric contaminants may disqualify many potential absorbers. Unfortunately, only a minute amount of information is available on the degradation of these coatings. Currently, it is hard enough to

obtain temperature stability information in dry air for a particular coating.

2. Tandem absorbers appear to be very popular and well suited for solar energy collection at moderate temperatures. Natural oxidation of metals shows promise of being a very simple selective absorber.

3. For electroplating there is a possibility of strip plating thin metal and bonding this material to collector plates, the strips being transported and sold in rolls. This technique is being used already on a small scale for black chrome. Automated sputtering also offers the advantage of accepting large work surfaces, with the ability to deposit a wide variety of substances. Improvements in vacuum systems and large scale production vacuum deposition techniques are also necessary for low cost and high yields.

4. Coatings should have their spectral properties designed to the optimum with respect to specific operating conditions and temperatures. Certain coatings should be matched to a particular collector design and end use. In many cases α , ϵ values should be designated as a function of temperature, to match end use temperature.

5. Multilayer coatings frequently exhibit corrosion and interdiffusion problems at elevated temperatures. An example that these problems may be overcome is demonstrated by the AMA absorber.

6. A solution to a manufacturing problem which must be worked out is the production of reproducible α and ϵ coatings values, along with collector standards and specific efficiency rating systems,

including the measurement of optical parameters of various coatings provided by the manufacturers.

7. Coatings are very important in terms of collector durability. If a coating degrades, so does the entire system. In a commercial or industrial application solar collectors can be maintained on a routine schedule. But for the homeowner this is seldom possible. What is needed are coatings which will not optically or thermally degrade much more than a few percent over the lifetime of the collector, possibly 10-30 years. In other words, hopefully the coating would not be the limiting factor of collector lifetime. These coatings would have to withstand the most severe conditions such as summer stagnation and temperature cycling for many cycles. Stagnation can occur early in a collector's lifetime, perhaps during the construction of a collector system. Once in operation solar collectors can stagnate when the system malfunctions; stagnation temperatures can exceed 200°C. Stagnation temperatures should be known, as an engineering design parameters for specific coating and collector designs. In general it is important that the coating be able to survive several weeks (months) of stagnation temperatures. Currently little is known about the effects of these short term high temperatures excursions on coating properties. This remains as one of the most significant areas of investigation. Humidity and potential outgassing of sealant and insulation used in collectors can have an adverse effect upon coating life and collector performance. All of these points need to be pondered and evaluated before a collector can exhibit the necessary reliability.

8. A formal materials cost analysis is needed for selective surfaces. The black chrome coatings range from \$7.50-\$12.00/m² which appear to be fairly typical of electroplated coatings. Commercial vacuum deposited selective coatings can cost from \$16.00-\$38.00/m² and upward. All of these numbers are just estimates; they do not represent high volume production with possible automation.

9. Work should be performed upon the toxicity of the various coatings used in collectors. Another concern is with possible flammability and toxic by-products of combustion generated from the burning of solar collectors in fires.

10. The amounts of energy used to make various coatings and collectors should be evaluated. For many coatings heat treatments or hot fluid baths are used. Electricity is needed in many cases for vacuum deposition, CVD, sputtering, plasma deposition and electroplating.

11. It is also necessary to consider the availability of raw materials used for coatings and collectors. Some materials are in very short supply or have already been allocated for specific usage in other manufacturing areas. At present, some metals such as chromium and tin are imported in the United States. Changes made by our suppliers could have an impact upon our society both economically and politically.

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Table 1. Optical tapping surfaces.

Type	a	e	a/e	Structure
Tungsten dendrite (IBM)	0.99	0.26-0.3 (550°C)	3.8-3.3	Aligned Dendrites
Aluminum--Steel (TI)	0.99	0.55 (26°C)	1.8	Random Dendrites
Aluminum--304 Stainless Steel (TI)	0.89	0.47 (26°C)	1.9	Random Dendrites
Aluminum--Nickel (TI)	0.94	0.30 (26°C)	3.1	Porous Cavities
4022 Al--201 Nickel (TI)	0.97	0.21 (26°C)	4.6	Porous Cavities
Aluminum--430 Stainless Steel (TI)	0.98	0.51 (26°C)	1.9	Random Dendrites
Nickel dendrite (LASL) on Aluminum	0.95	0.6 (100°C) 0.71 (100°C)	1.6 1.3	Rounded- Aligned Dendrites

Source: Refs. IBM [7], TI [10] and LASL [45].

Table 2. Summary table of selective surface. The following table was compiled for selected solar absorber coatings. All temperatures are °C, listed in parenthesis.

Material	Fabrication Technique	α	(Low T)	(High T)	Stability °C	Ref.
Al	Anodized, $KMNO_4$	0.80	0.35(100)			46
Al	Alcoa 65, Electrode.	0.93	0.35		>163	47
Au	Gas. Evap.	0.99	0.1		100	48
Ge	Gas. Evap.	0.91	0.2(160)	0.5(350)		46
Ge	Vac. Evap.	0.61	0.54(240)	0.54(240)		46
Ge	Paint (silicone binder)	0.91	0.8(200)			46
Ni	CVD Dendrites	0.95	0.3(100)- 0.6(100)			45
α -Si (on Mo)	CVD	0.77	0.1 est.			49
Si	Paint	0.83	0.7(200)			46
Si (on Ag)	CVD+AR coat	0.80	0.05(100)	0.07(500)	500(V)	7
W	CVD Dendrites	0.80- 0.96	0.1(100)		500	8
Zn	Anodized	0.95(AM2)	0.08(60)			34
Steel	Chem. Conv. (Fe_3O_4)	0.83(AM2)	0.06(60)			34
Steel	Acid Dip	0.91	0.1(100)		200	29
Steel	Chem. Conv. (Fe_3O_4)	0.90	0.07(90)	0.35(200)		46
S. Steel	Conversion	0.93	0.11			50
S. Steel	Chem. Conv.	0.91				46
S. Steel	Therm. Oxide	0.82	0.15			46
CuO_x	Chem. Conv.	0.91	0.16(<100)	0.4(200)		46*
CuO	Sol. Etch. Al-Cu	0.93	0.11			61*
CuO_x	Chem. Spray	0.93	0.11(80)			46*
Cu_2S	Chem. Conv.	0.79	0.2(200)			46*
CoO_x	Anod. Co Electrode.	0.93	0.24(260)			51†

Table 2. Continued.

Material	Fabrication Technique	a	(Low T)	(High T)	Stability °C	Ref.
CoO _x	Electrod. + Heat T.	0.87 (AM2)	0.07(60)			34 [†]
Co ₃ O ₄	Thermal oxide	0.90	0.3(140)		>1000	46 [†]
FeC _x	DC Reac. Sput.	0.80	0.02(150)		<350	52
HfC	Intrinsic	0.65	0.1(100)			3
PbS	Vac. Deposit.	0.98	0.2(240)	0.3(300)	300	46
PbS	Paint (Silicone binder)	0.94	0.8(200)			46
PbS	Paint	0.90	0.4(100)			3
PbO ₂	Electrodeposit	0.98				53
F doped SnO ₂	Paint	0.92	0.14		200	54
WO ₃	RF Sput. on Ni	0.83(AM2)	0.07(60)			34
Al ₂ O ₃ +Ni	Evap. Composite	0.94	0.10(150)	0.35(500)		55
Al ₂ O ₃ +Pt	Evap. Composite	0.94	0.07(150)	0.3(500)		55
Al ₂ O ₃ +Au	Sputtered	0.95	0.025(20)		300	56
Al ₂ O ₃ +Cu	Sputtered	0.9	0.045(20)		200	56
Al ₂ O ₃ /ZrC _x N _y	React. Sput. (on Ag.)	0.91	0.05	175(A),700(v)		54
CaF ₂ +Si	Sputtered	0.7	0.1			54
CaF ₂ +Ge	Sputtered	-	-			54
CrO _x ² +Cu	Paint	0.92	0.30(100)			7
CrO _x -Cr	Electrod. (on Ni)	0.95	0.07(100)		350	11 [§]
CrO _x -Cr	Electrod. (on Sn)	0.97	0.06			57 [§]
CrO _x -Cr	Electrodeposit	0.95	0.10(100)	0.2(350)		21 [§]
Cr ₂ O ₃ +Cr	RF Sputtered	0.92	0.08(121)		300	17
Cr ₂ O ₃ +Co	Plasma Spray	0.90(800)		0.5(800)	800	46
(Cr-Ni-Va)O _x	Electrodeposit.	0.94	0.40(260)			51

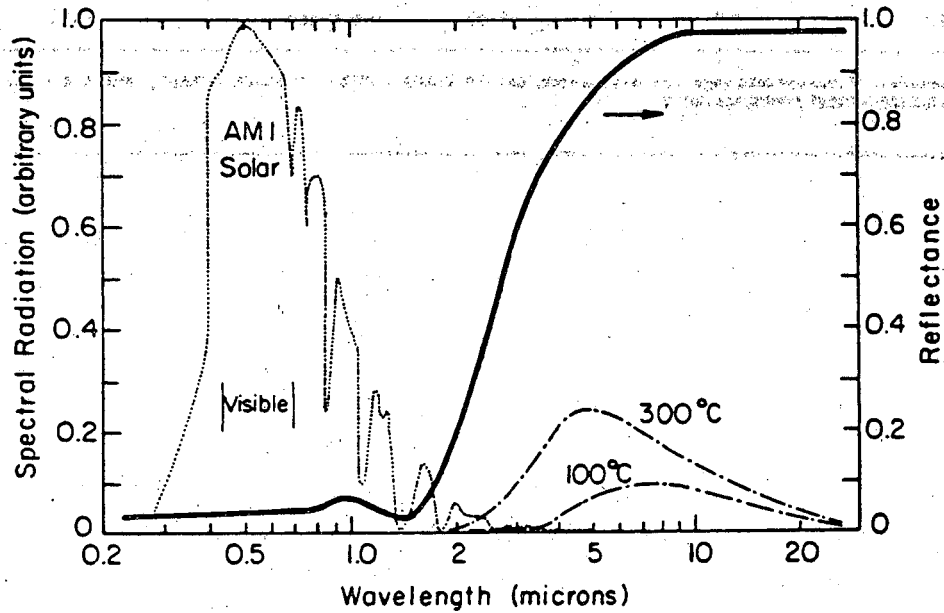
Table 2. Continued.

Material	Fabrication Technique	α	(Low T)	(High T)	Stability °C	Ref.
CuO/Au	Paint	0.8	0.06		> 600	54
CuO/Ag/Rh ₂ O ₃	Paint	0.9	0.1		< 400	48
CuO+Fe+Mn	Paint dip	0.92	0.13(100)		> 150	54
In ₂ O ₃ +Si	Vac. Evap.	0.85	0.07			35
MgO+Au	RF Sputtered	0.93	0.1		< 300	48
NiS-ZnS	Electrodep.	0.88	0.1(100)	0.16(300)	< 220	46
NiS-ZnS	Electrodep. 2 layer	0.96	0.07(100)		< 280	36 [†]
NiS-ZnS	Electrodep. 3 layer	0.91	0.14			48 [†]
NiS-ZnS	Electrodep. on zinc	0.94	0.09(100)		< 200	58 [†]
Si ₃ N ₄ /Mo	CVD	0.82	0.08			59**
W ₃ /W	CVD dendrite	0.90	0.18		< 223	9
WC+Co	Plasma Spray	0.95(600)	0.28(200)	0.4(600)	> 800	46
Electroblack	Electrodep.	0.86	0.05			60
Maxorb	-	0.97	0.10		150	48
Solarox	Electrodep.	0.92	0.20		200	48
Solartex	Electrodep.	0.95	0.16(310)		700	48
Al/Ce/SiO	Vac. Evap.	0.79	0.012(100)			62
Al/PbS/SiO	"	0.89	0.018(100)			62
Ni/Ce/SiO	"	0.88	0.035(100)		240(A)	62
Ni/PbS/SiO	"	0.93	0.043(100)			62
Cr/Ce/SiO	"	0.93	0.11(100)		240(A)	62
Cr/PbS/SiO	"	0.94	0.12(100)		240(A)	62
SiO/Cr/SiO	"	0.88	0.1		< 450	46
Ag/Al ₂ O ₃	"	0.70-0.75	0.1			39
Al ₂ O ₃ /Mo/Al ₂ O ₃	"	0.85-0.95	0.34(100)	0.11(500)	> 550	63

Table 2. Continued.

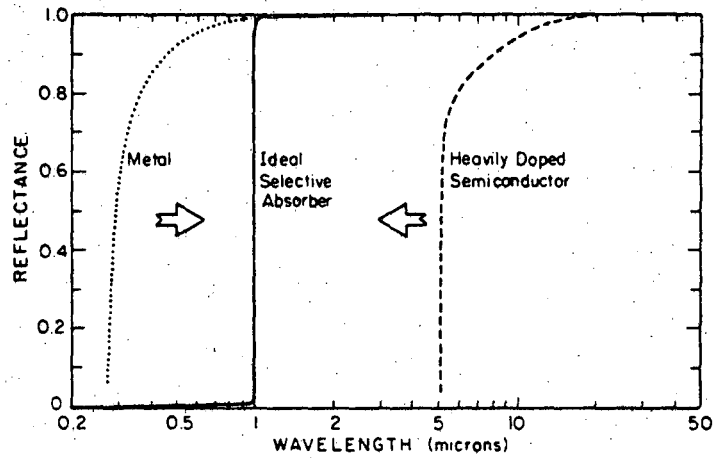
Material	Fabrication Technique	a	(Low T)	(High T)	Stability °C	Ref.
MgF ₂ /Sn (part.)	"	0.95	0.01			5
Ag/Cu _x S	"	0.90	0.1			39
OCLI	"	0.95	0.05(100)		>300	64

Several of these coatings are also known as: * BLACK COPPER, † BLACK COBALT, ‡ BLACK CHROME,
 § BLACK NICKEL, **BLACK MOLY.



XBL 775-5462A

Fig. 1. Wavelength relationship between a characteristic solar selective surface in terms of reflectivity, to that of the solar energy (AM1) and blackbody spectra (100°C, 300°C).



XBL 793-5887

Fig. 2. Reflectance of an ideal selective absorber compared to that of an idealized metal and heavily doped semiconductor (after Seraphin [1]).

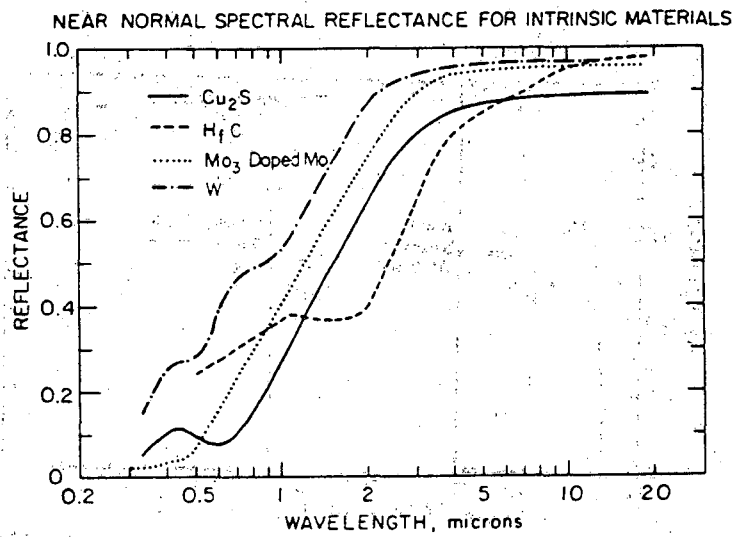
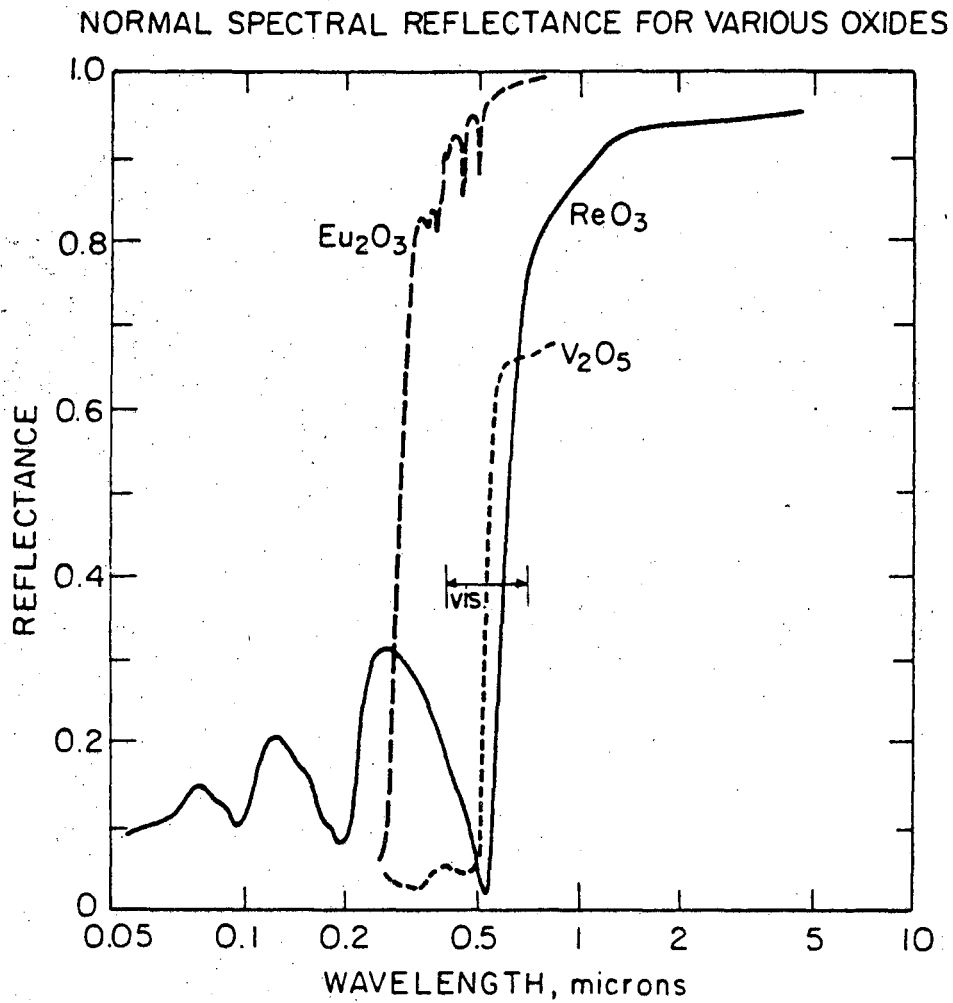


Fig. 3. Spectral reflectance for intrinsic materials Hafnium carbide, metallic tungsten, and MoO₃ doped Mo, B. O. Seraphin [1], and semiconductor Cu₂S, Meinel and Meinel [2].



XBL783-4706

Fig. 4. Spectral reflectance of various oxides compiled by Touloukian et al. [6] showing intrinsic selectivity for dieuropium trioxide, rhenium trioxide single crystal and divanadium pentoxide.

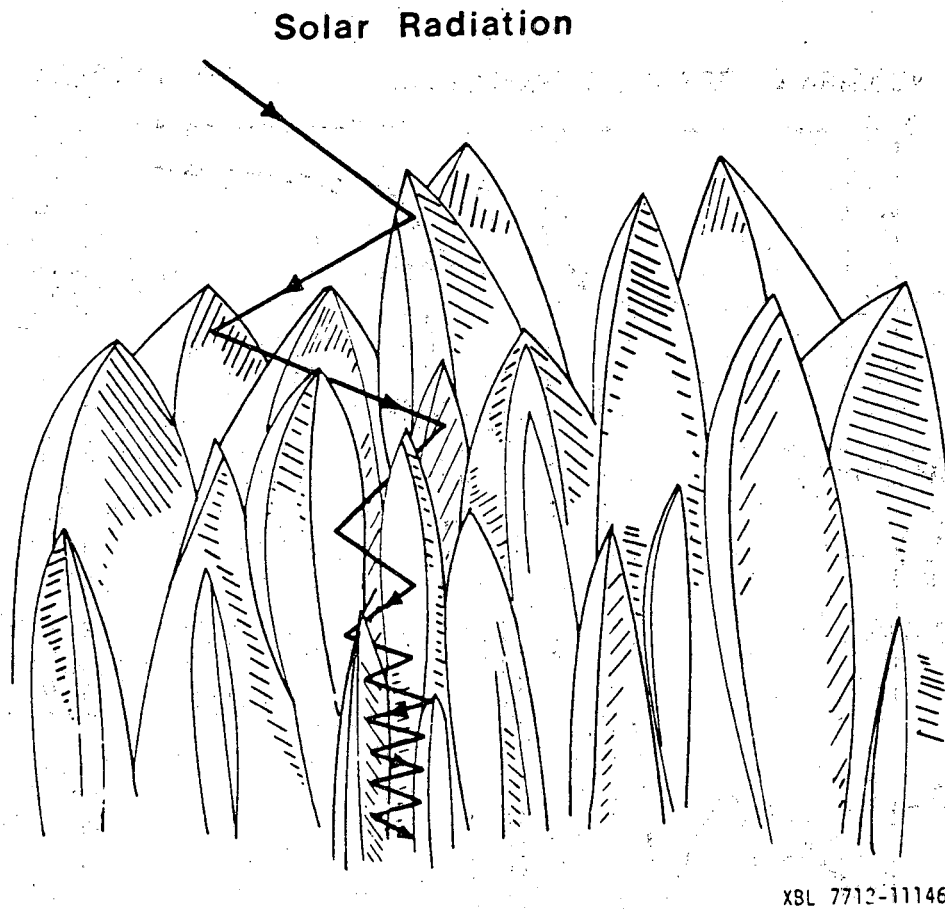
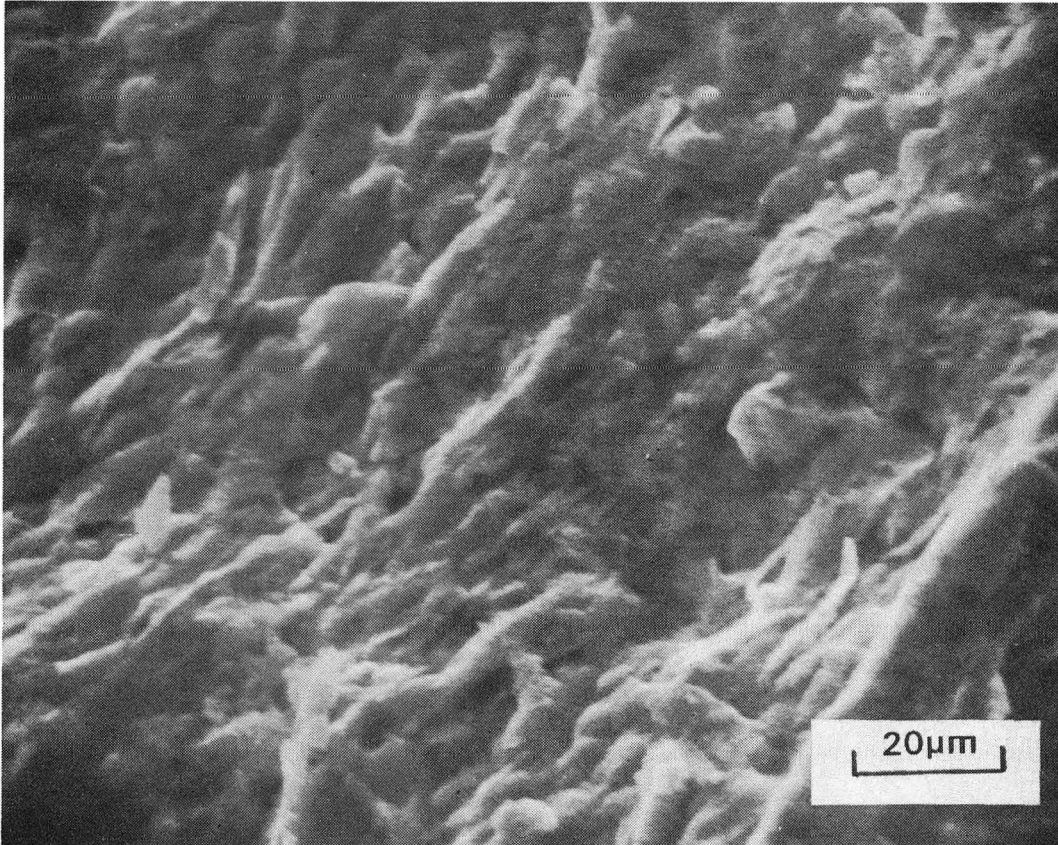
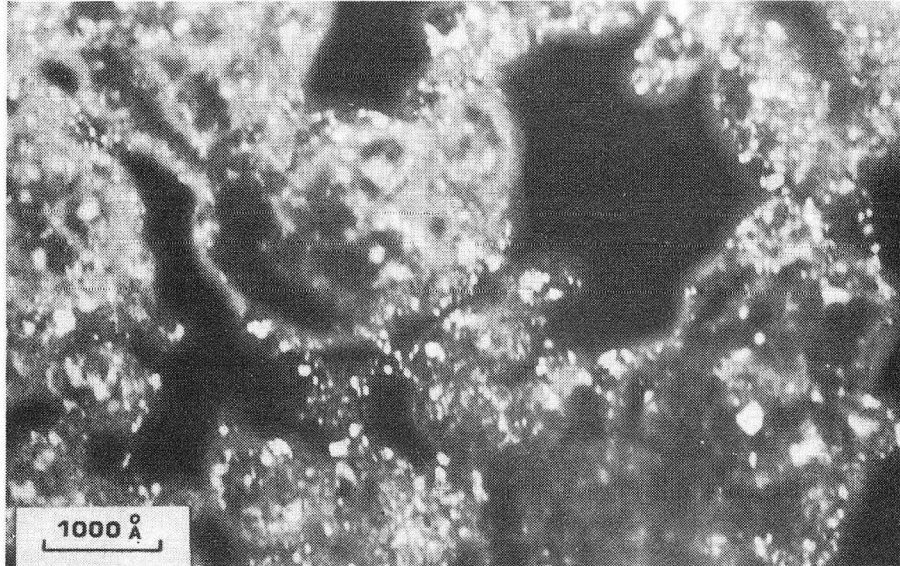


Fig. 5. Schematic representation of a dendritic selective surface. Incoming radiation can average up to fifty reflections before being completely absorbed.



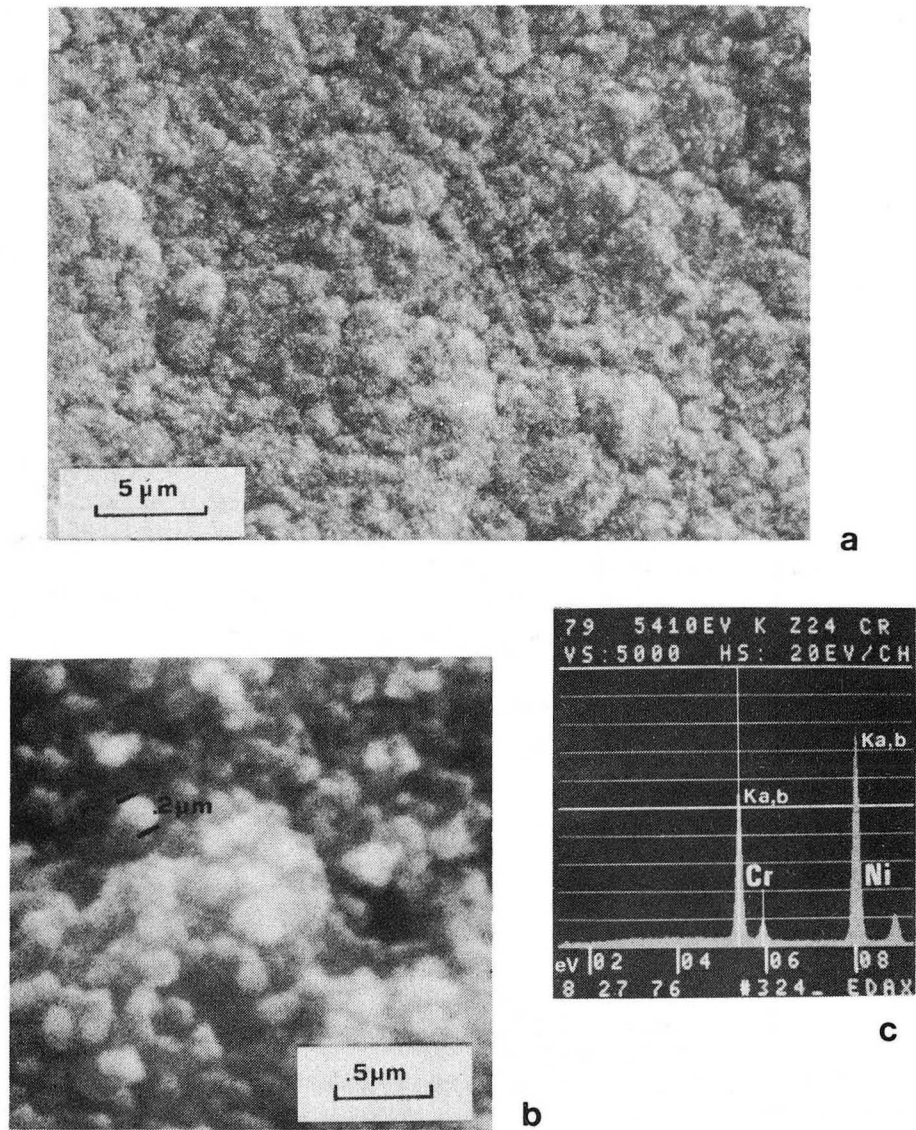
XBB 7811-13942

Fig. 6. Surface showing solar selectivity by exhibiting a dendritic fine structure of the size order of the wavelengths absorbed, for the 4022 Aluminum/201 Nickel absorber. This surface was formed by reacting metallic laminated layers bonded directly to collector panels. (Photo credit: T. Santala and R. Sabol, Texas Instruments).



XBB 774-3545

Fig. 7. Agglomeration of chromium particles with matrix material viewed by transmission electron microscopy. This dark field shows metallic chromium particles as bright spots. Mean particle diameter is 140\AA according to Lampert [11].



XBB 778-8007

Fig. 8. Typical surface microstructure of black chrome on nickel plated copper examined by scanning electron microscopy by Lampert [11]. (a) Typical surface microstructure, (b) detail of particles, (c) EDAX of region (b), showing chromium and nickel as principal constituents.

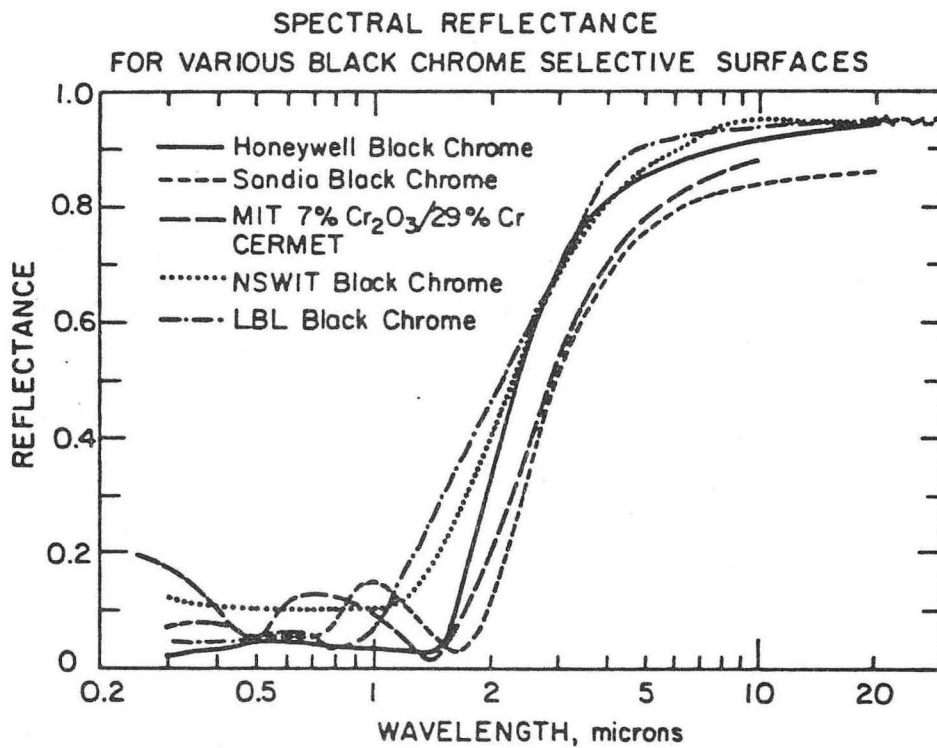
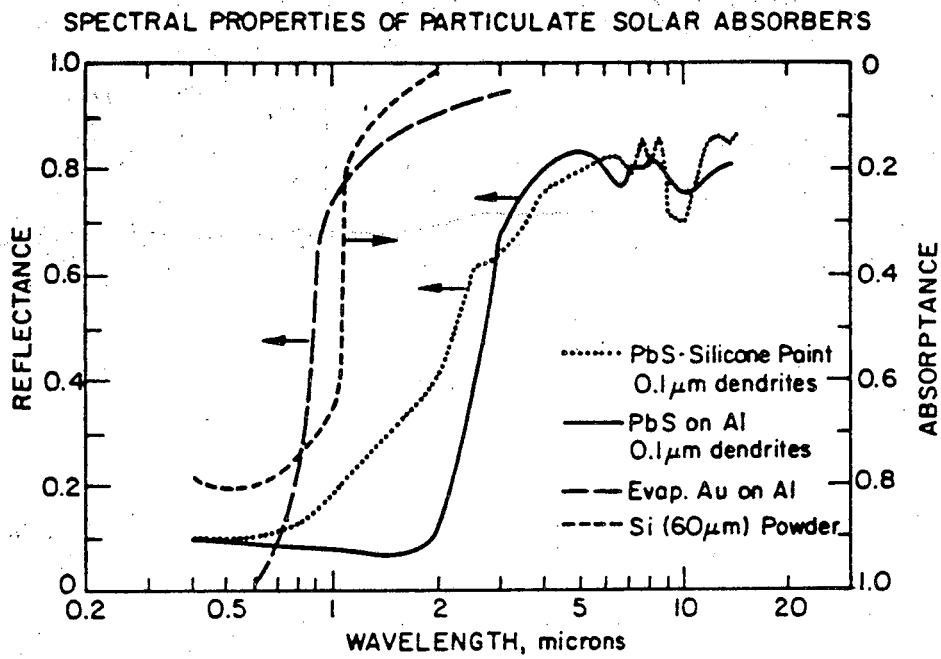
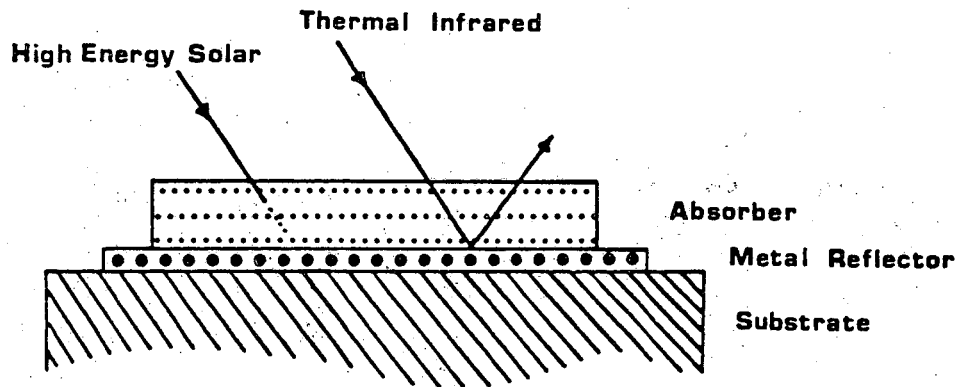


Fig. 9. Reflectance for different types of Black Chrome surfaces, including the Honeywell (Masterson et al. [18]), Sandia and New South Wales Institute of Technology (Driver et al. [19]) and LBL (Lampert [11]) electroplated surfaces. The MIT cermet [17] is shown for comparison.



XBL 783-4723

Fig. 10. Reflectance for particulate absorbers consisting of PbS, Williams et al. [23], evaporated gold on aluminum, Lee [27] and silicon powder coatings, Warren [25].



XBL 7712-11145

Fig. 11. Schematic cross section of a semiconductor-metal tandem selective absorber.

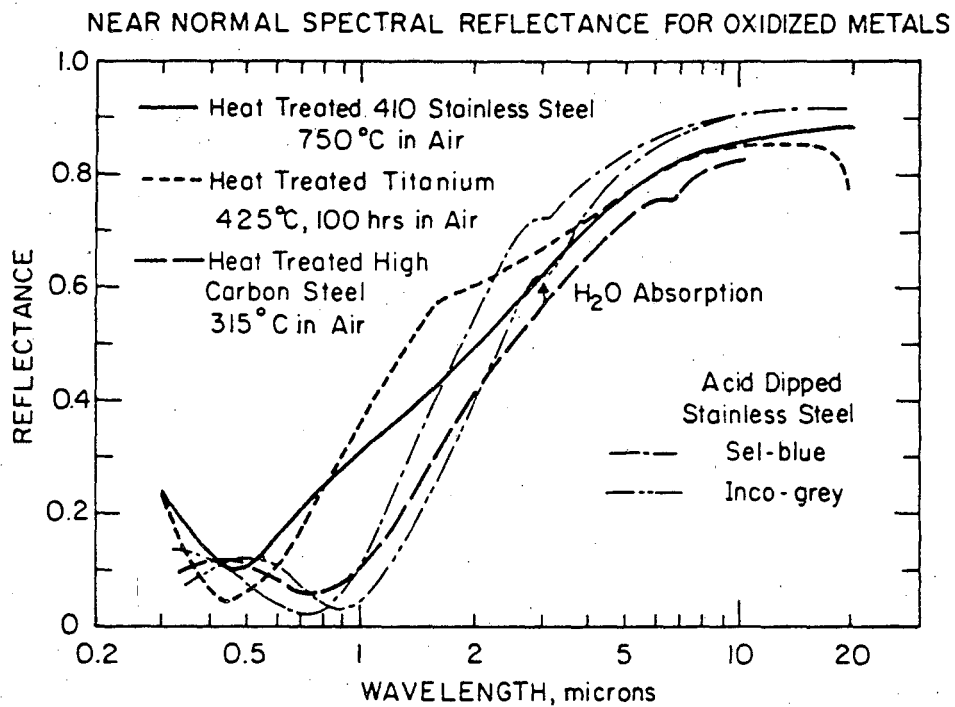


Fig. 12. Reflectance of natural oxides found on stainless steel and titanium, Edwards et al. [28]. Acid treated stainless steel shown for both Inco and SEL processes investigated by Karlsson and Ribbing [29]. A heat treated mild carbon steel is shown for comparison, Borzoni [30].

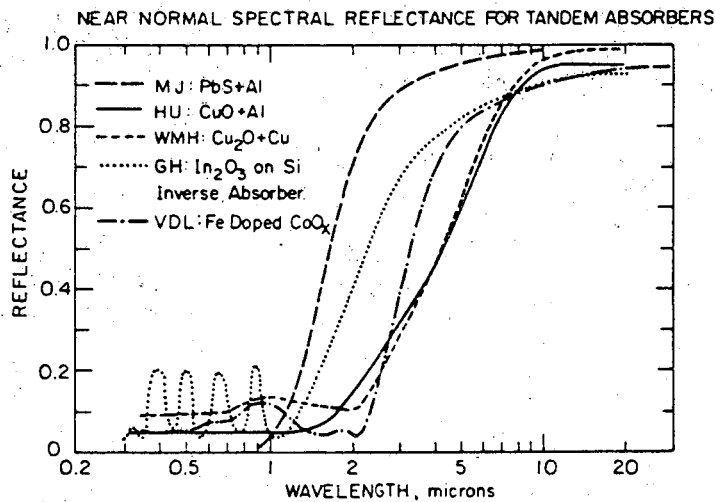
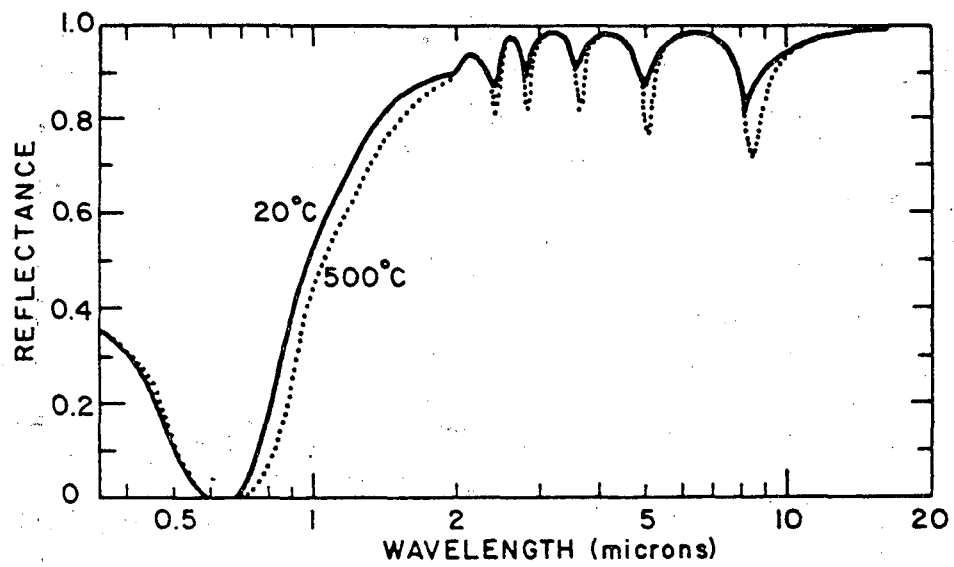


Fig. 13. Reflectance of various tandem absorbers--lead sulfide on aluminum, McMahon and Jaspersen [31], copper oxide on aluminum Hottel and Unger [32], Cu_2O on copper, Watson-Munrd and Horwitz [33] thermally converted Fe doped CoO_x , Van Der Leij [34] and an inverse absorber In_2O_3 on Si. The In_2O_3 layer acting like an infrared reflector while the buried silicon layer performs as a solar absorber, Goldner and Haskal [35].



XBL7711-10845A

Fig. 14. Near normal reflectance of a silicon photothermal absorber, designed by the University of Arizona Masterson and Yoder [36]. This type can withstand temperatures in excess of 500 C.

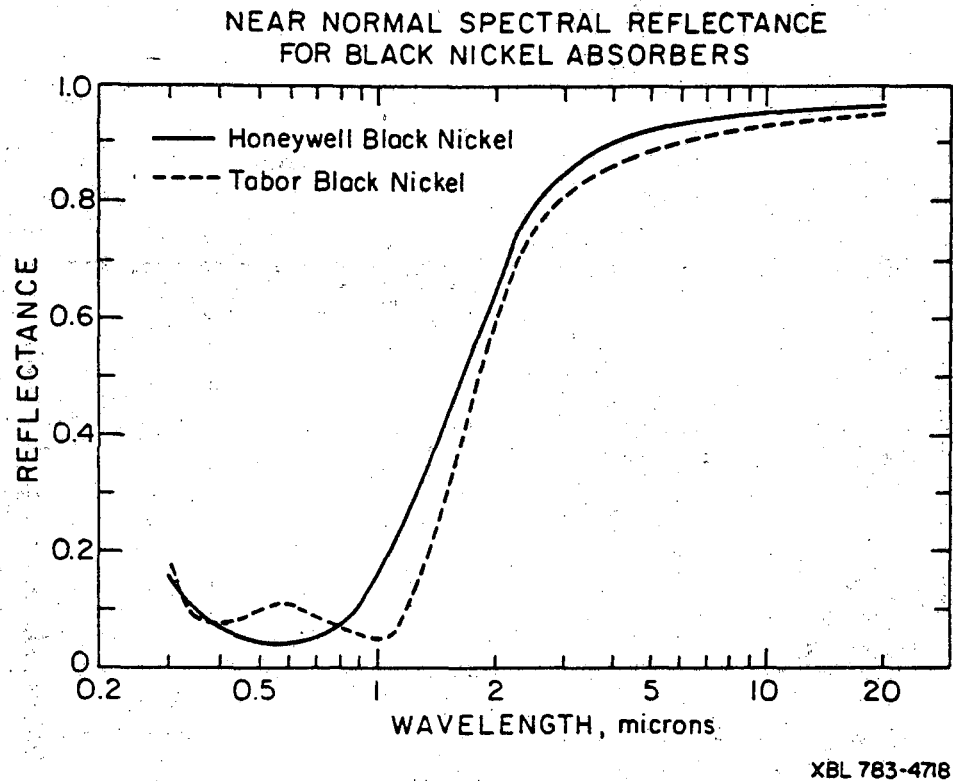
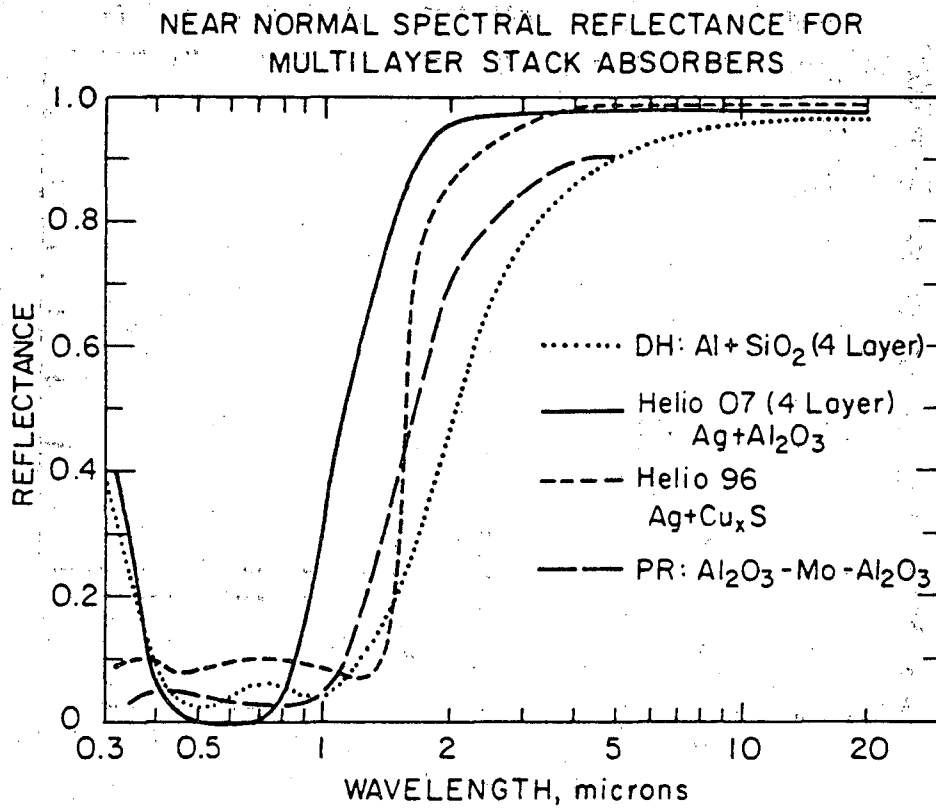
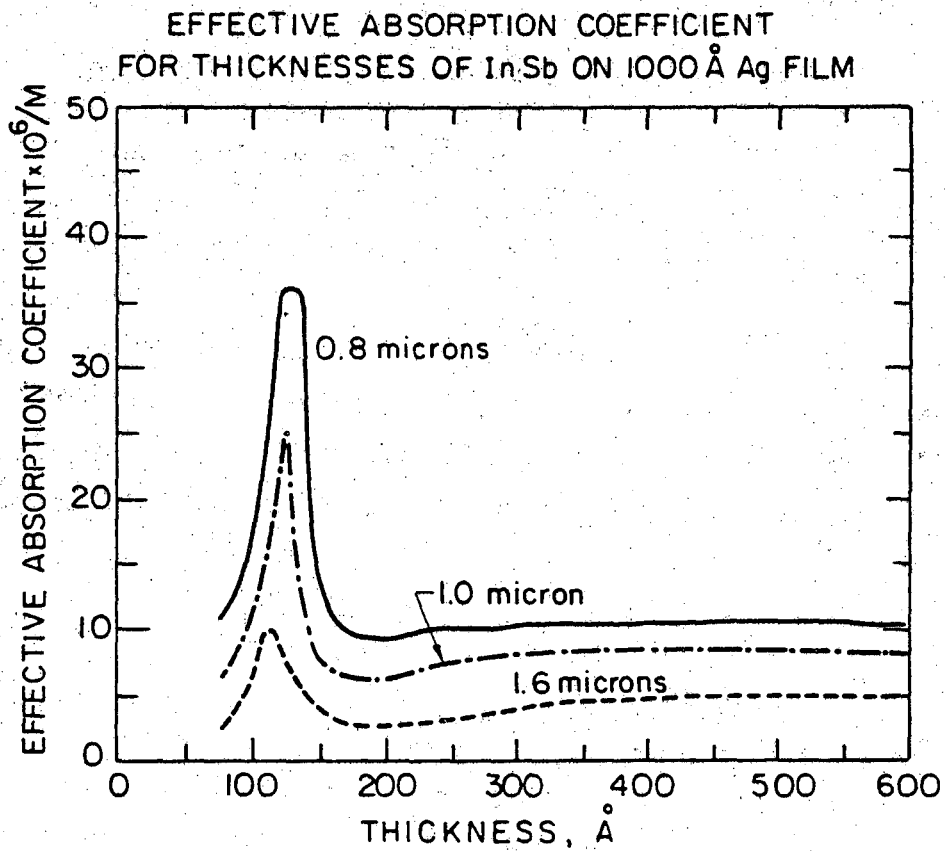


Fig. 15. Spectral reflectance for two types of black nickel. The recent coating is the Honeywell (Mar et al. [37]) type after being developed by Tabor [38].



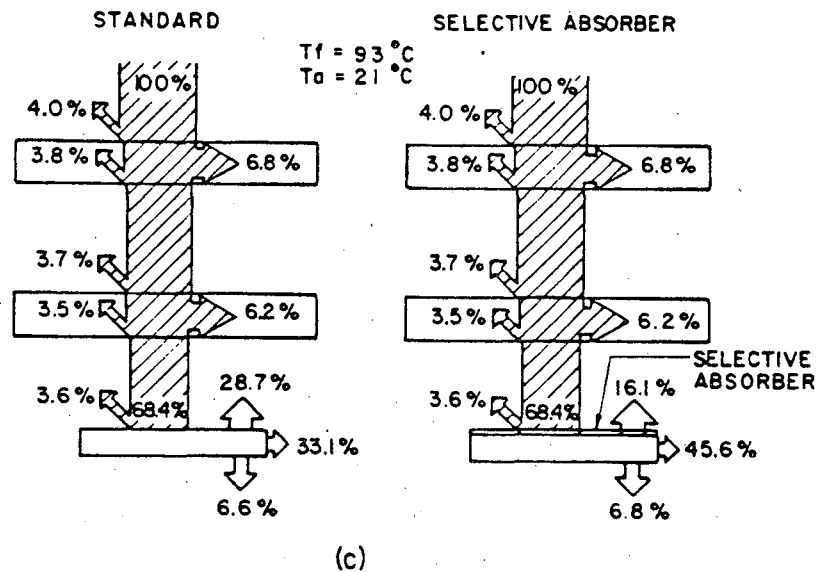
XBL792-5789

Fig. 16. Reflectance for three types of multilayer absorbers. Two Heilo types, Meinel et al. [39], are shown for comparison to the Honeywell high temperature absorber, Peterson and Ramsey [40]. Also the reflectance for a classic four layer absorber of SiO₂ on aluminum is depicted, Drummeter and Hass [41].



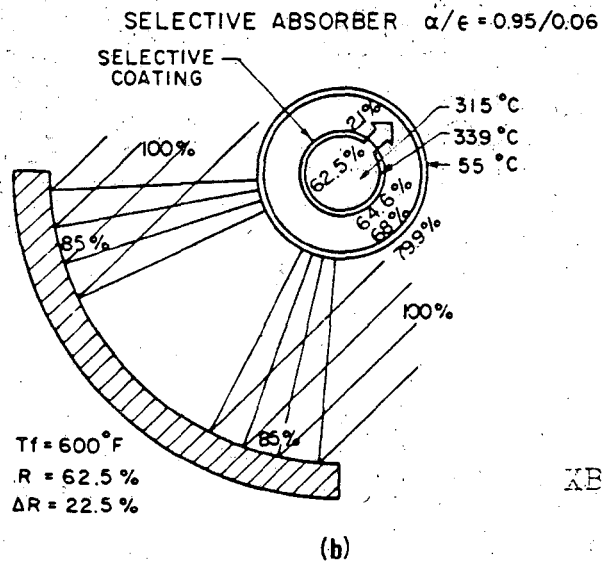
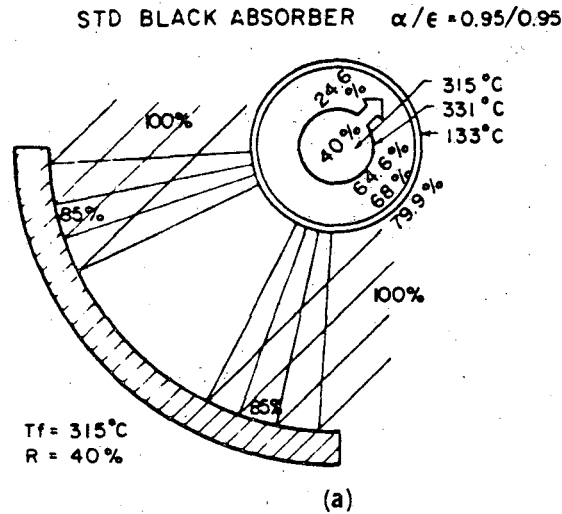
XBL 792-5785

Fig. 17. The effective absorption coefficient for different thicknesses of InSb on 1000Å of silver, for various values of incident radiation Burrafato et al. [42] .



XBL 781-6856D

Fig. 18. The effect of using a selective absorber compared to a non-selective type on collection efficiency for a flat plate collector, operating at 93°C (200°F) with ambient temperature of 21°C (70°F). The non-selective surface has $a = 0.92$ and $e = 0.92$ (93°C), and the selective surface has $a = 0.9$ and $e = 0.1$ (73°C) (after Winegardner [43]).



XBL 781-6857F

Fig. 19. The effect of using a selective absorber compared to a non-selective one for a concentrating parabolic operating at 315°C (600°F) with ambient temperature of 21°C (70°F). Notation: (R) Net collection efficiency, (ΔR) change in collection efficiency over that of a standard black absorber (after Winegardner [44]).

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