CET IIA

Materials and Corrosion
Corrosion and Material Selection: Part II

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Worksheet 2 Solutions

Question 8

The purpose of this question is to gain knowledge of the 8 local corrosion mechanisms. So far we have worked under the assumption that corrosion is uniform, which is often not the case. Chapter 3 in Corrosion Engineering by Fontana and Greene covers these mechanisms in detail. It is important to be able to recognise the CHARACTERISTICS, MECHANISMS and ways of PREVENTING each type of corrosion.

Galvanic Corrosion

CHARACTERISTICS	Metals in contact - Galvanic Corrosion of Al
MECHANISMS	The metals are in electrical contact, so electrons flow between them.
PREVENTING	Insulate the metals or use ones close to each other in the relevant galvanic series

Crevice Corrosion

CHARACTERISTICS	Rapid localised corrosion due to stagnant fluids in crevices.
MECHANISMS	Oxygen is depleted in crevices, creating a small anode of the crevice. This leads to rapid dissolution of the metal. The positive charge attracts chloride ions which react with the metal and water to produce hydrogen and chloride ions which accelerate corrosion.
PREVENTING	Close crevices. Regular equipment inspection.

Pitting

CHARACTERISTICS	Similar to crevice corrosion. Differs only in the way the crevice or 'pit' is formed.
MECHANISMS	Usually form in direction of gravity. They are generated by dislocations, differences in composition.
PREVENTING	Same as for crevice corrosion.

Intergranular Corrosion

CHARACTERISTICS	Occurs when metals are prepared by quenching. Precipitates form at the grain boundaries.
MECHANISMS	When a metal is quenched and reheated precipitates form . These can take out certain elements of the alloy which affects the corrosion resistance of that area of the metal.
PREVENTING	Keep carbon content of metal low. Quenching rapidly dissolves precipitates. Can also include other metals in the alloy which will form carbides preferentially.

Erosion Corrosion

CHARACTERISTICS	
MECHANISMS	
PREVENTING	

Selective Leaching

CHARACTERISTICS	Reduces the strength of an alloy.
MECHANISMS	An element is removed from the alloy by galvanic corrosion.
PREVENTING	Add a stabilising additive.

Stress Corrosion

CHARACTERISTICS	Simultaneous effects of corrosive environment and a static/varying stress.
MECHANISMS	
PREVENTING	

Hydrogen Damage

CHARACTERISTICS	
MECHANISMS	H atoms formed by dissociation of H_2 at metal surfaces. H atoms are so small that they can diffuse through the metal.
PREVENTING	Choose FCC metals over BCC.

Question 9

Part *(a)*

The charge when one kilomole of a substance reacts is

$$\begin{aligned} Q &= nF \\ &= 2 \times 9.648 \times 10^7 \\ &= 192,960,000 \text{ C kmol}^{-1} \ . \end{aligned}$$

There are 65 kg of Zn per kmol, so the charge created per kg of Zn oxidised is 2,890,000 C.

Part *(b)*

$$\begin{aligned} \frac{Q}{m} &= 2,890,000 \text{ A.s} \\ \text{m.w.r} = \frac{m}{Q} &= \frac{1}{2,890,000} \text{ kg A}^{-1} \text{ s}^{-1} \\ &= 10.9 \text{ kg A}^{-1} \text{ yr}^{-1} \ . \end{aligned}$$

Question 10

Part *(a)*

The blocks have an area of $\frac{\pi dl}{2} = 0.079 \text{ m}^2$. To prevent corrosion we need $120 \times 10^{-3} \times 3200 = 384$ A of current.

C-SENTRY: Current output $= 0.079 \times 6.5 = 0.514$ A per block therefore we need $\frac{384}{0.514} = 748$ blocks.

GANVALUM I: Same as for C-SENTRY.

GALVOMAG: Current output $= 0.079 \times 10.8 = 0.853$ A per block therefore we need $\frac{384}{0.853} = 450$ blocks.

Part *(b)*

To get the volumetric wastage rate, use the following relation based on comparing dimensions:

$$\text{Volumetric Wastage Rate} = \frac{\text{Mass Wastage Rate}}{\rho} \times 384 \text{ A}$$

C-SENTRY: V.M.R $= 0.58 \text{ m}^3 \text{ yr}^{-1}$.

GANVALUM I: V.M.R $= 0.46 \text{ m}^3 \text{ yr}^{-1}$.

Galvomag: V.M.R $= 0.89$ m^3 yr^{-1}.

Part *(c)*

c-sentry: 5.8 m^3 will disappear over 10 years, therefore 1.93×10^{-3} m^3 will disappear from each block over ten years.

Each block has a volume of

$$\frac{\pi d^2 l}{8} = 1.96 \times 10^{-3} \text{ m}^3 \ .$$

So the new volume after ten years will be $1.96 \times 10^{-3} - 1.93 \times 10^{-3} = 3 \times 10^{-5}$ m^3. The final diameter will be

$$\begin{aligned} \frac{\pi d^2 l}{8} &= 3 \times 10^{-5} \text{ m}^3 \\ d &= 0.012 \text{ m} \ . \end{aligned}$$

Ganvalum I: $d = 0.047$ m.

Galvomag: There will be none left.

Part *(d)*

c-sentry: Work out the total amount of current thrown out and check it is greater than the minimum required to prevent corrosion (384 A). The total area of all the blocks will be

$$\begin{aligned} \text{Area} &= 3000 \times \frac{\pi d_{final} l}{2} \\ &= 28 \text{ m}^2. \end{aligned}$$

So the current created is $28 \times 6.5 = 184$ A, which is below the minimum required to prevent corrosion.

Ganvalum I: The total current thrown out is 720 A, which is sufficient.

Galvomag: There is none left.

Part *(e)*

We will use Ganvalum I, so the volume added by 3000 of these anodes is

$$\begin{aligned} V &= \frac{\pi d^2 l}{8} \\ &= 1.96 \times 10^{-3} \text{ m}^3 \ . \end{aligned}$$

3000 blocks will have a volume of 5.89 m^3. Multiplying by the density gives the additional mass through use of these anodes, which is 15,875 kg.

Question 11

Part *(a)*

The Tafel equations for each line are:

$$\frac{E_{0,c} - E_{corr}}{\log_{10}\left(\frac{i_{corr}}{i_0}\right)} = -\beta_c = |\beta_c| \tag{1}$$

$$\frac{E_{corr} - E_{0,a}}{\log_{10}\left(\frac{i_{corr}}{i_0}\right)} = \beta_a = |\beta_a| \ . \tag{2}$$

Summing the two gives:

$$\begin{aligned} \frac{E_{0,c} - E_{0,a}}{\log_{10}\left(\frac{i_{corr}}{i_0}\right)} &= |\beta_a| + |\beta_a| \\ \Rightarrow \log_{10}\left(\frac{i_{corr}}{i_0}\right) &= \frac{E_{0,c} - E_{0,a}}{|\beta_a| + |\beta_a|} \ . \end{aligned}$$

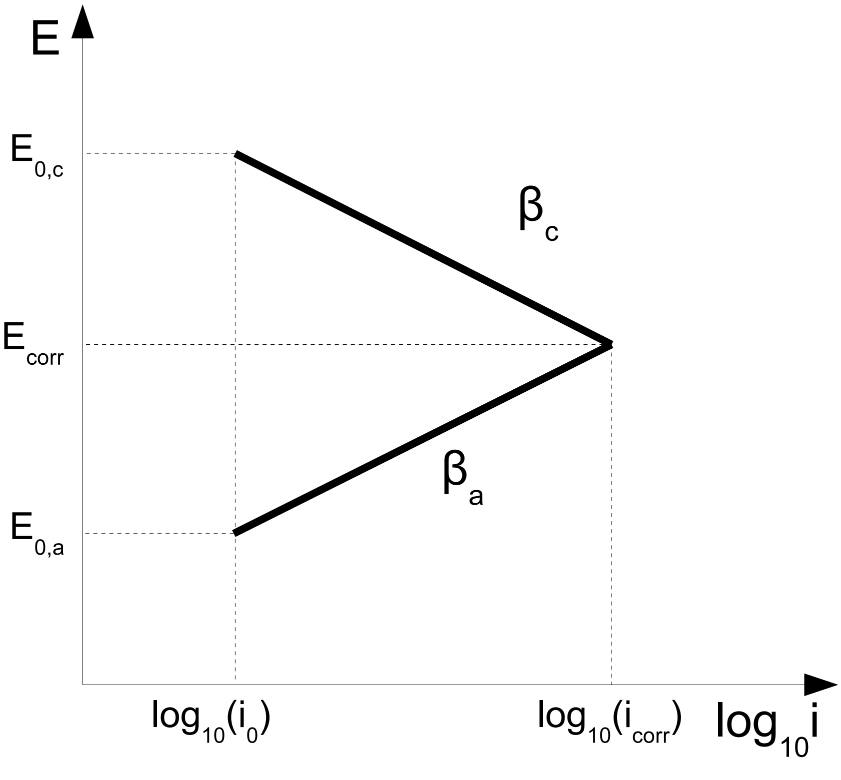


Figure 1: *Evans Diagram for Q11a.*

Part *(b)*

See Figure 2 for the corresponding Evans diagram.

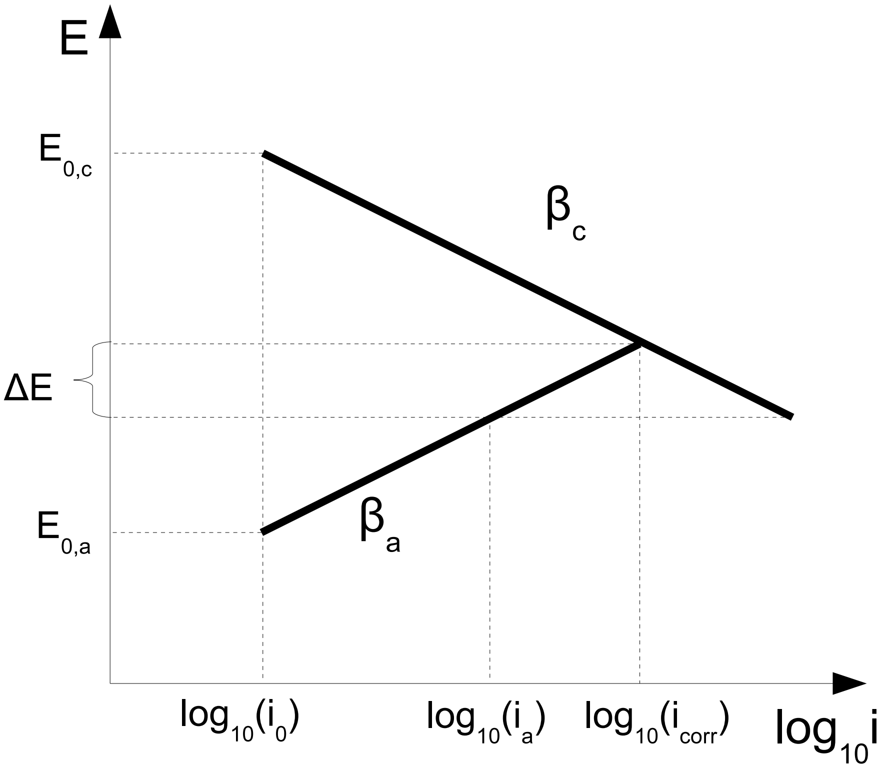


Figure 2: *Evans Diagram for Q11b.*

$$|\beta_a| = \frac{\Delta E}{log_{10}\left(\frac{i_{corr}}{i_{a,new}}\right)} \tag{3}$$

If $\Delta E = 0.05$ V and $\beta_a = 0.1$ V then

$$\begin{aligned} |\beta_a| &= \frac{0.05}{log_{10}\left(\frac{i_{corr}}{i_{a,new}}\right)} \\ \Rightarrow log_{10}\left(\frac{i_{corr}}{i_{a,new}}\right) &= \frac{0.05}{0.1} \\ \Rightarrow i_{a,new} &= 0.32 i_{corr}\ . \end{aligned}$$

So there is a 68 % reduction in corrosion rate.

Question 12

Part *(a)*

Paint it. Keep it clean and dry. Keep it lubricated.

Part *(b)*

Use inhibitors as the system is in a closed loop; the inhibitors will not need topping up.

Question 13

The mechanism for the oxidation reaction follows a parabolic growth (plot $(\Delta x)^2$ against t) law. This implies that the reaction is limited by the diffusion of ions and electron through the oxide layer.

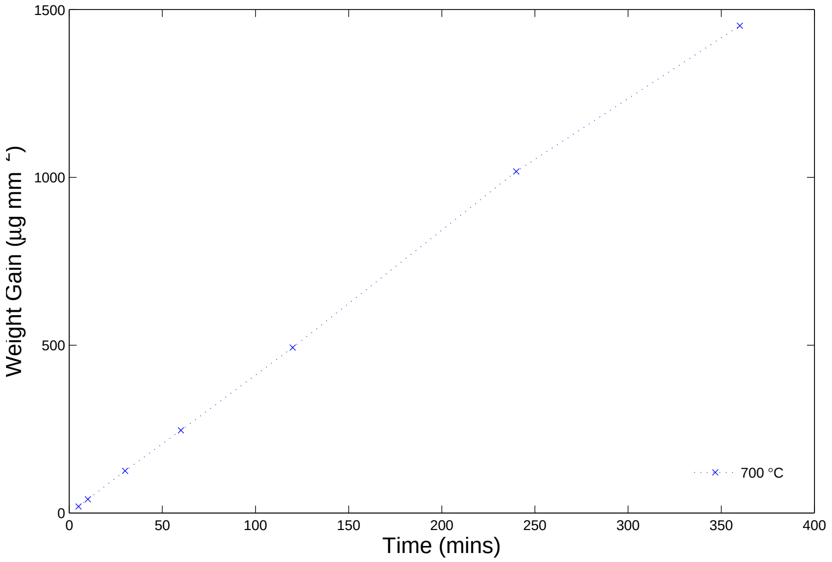


Figure 3: *Oxide growth rate for Q13a. The square of the weight gain is plotted against time.*

Part *(b)*

Some types of metal ions may occupy metal vacancy sites which will slow down diffusion, whereas some may increase the number of metal vacancy sites and therefore increase the rate of diffusion. Lower diffusion rates give lower rates of metal loss.

Part *(c) (i)*

If the oxide layer becomes brittle the oxide may break off and expose the underlying metal. This will temporarily increase the rate of oxidation until the oxide layer is reformed.

Part *(c) (ii)*

The growth rate will follow a logarithmic law. This is because at lower temperatures the rate of diffusion within the oxide layer is slow.

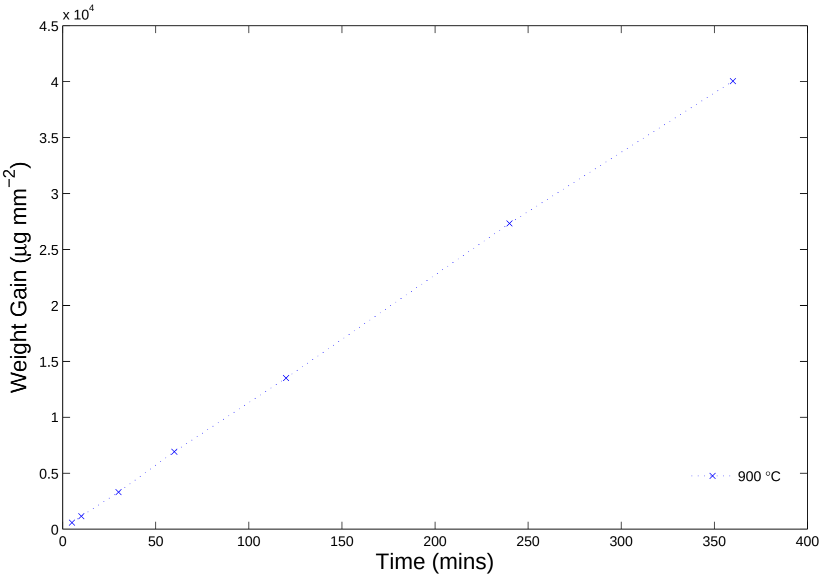


Figure 4: *Oxide growth rate for Q13b. The square of the weight gain is plotted against time.*

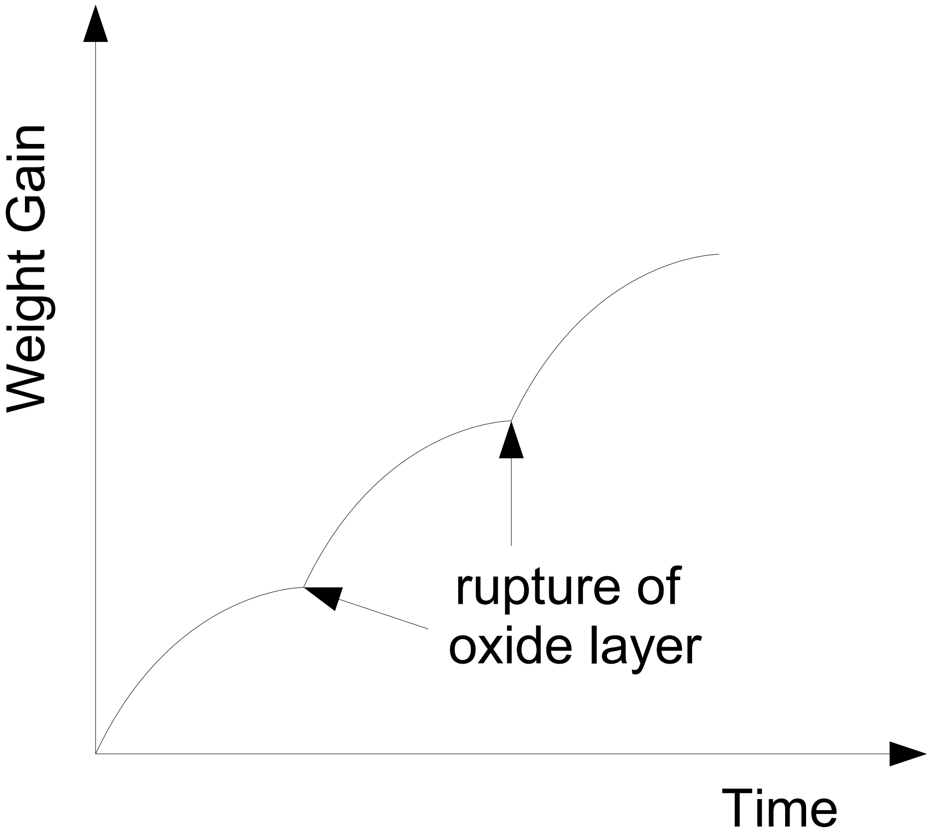


Figure 5: *Oxide growth rate for Q13c.*

Question 14

	COST	UTILITY	STRENGTH	CORROSION RESISTANCE
CARBON STEEL	Cheap	Easy to make and use. Quite strong	Brittle at cold temp. and oxidises at high temp.	Corrodes easily in many environments
STAINLESS STEEL (AUSTENITIC)	Expensive	Easy to make	Very strong	Excellent
COPPER	Expensive	Good thermal conductivity	Good	Oxidation at high temp. can occur and it corrodes in acids
GLASS-LINED CARBON STEEL	Cheap	Difficult to shape	Brittle	Excellent

Question 15

Part *(a)*

Define the objective function and constraints:

$$\begin{gathered} \min\,(m) \\ m \in \mathbb{R}^+ \end{gathered}$$

where m is the mass of the oar. If the oar has length L, radius r and density ρ then the mass of the oar will be (approximating the shape as a cylinder)

$$m = \rho \pi r^2 L \ . \tag{4}$$

The stiffness of the oar is given as

$$S = \frac{6\pi E r^4}{L^3} \ . \tag{5}$$

The length and stiffness of the oar are specified, so for any given material the radius of the oar will be fixed by the stiffness equation. Rearranging the stiffness equation gives

$$r^2 = \sqrt{\frac{SL^3}{6\pi E}} \ . \tag{6}$$

Substituting this into the equation for the mass of the oar gives

$$\begin{aligned} m &= \rho L \pi \sqrt{\frac{SL^3}{6\pi E}} \\ m &= \frac{L^{\frac{5}{2}}\sqrt{\pi S}}{6} \frac{\rho}{\sqrt{E}} \ . \end{aligned}$$

The only unknowns in this equation are ρ and E. To minimise m, we therefore need to maximise $\frac{\sqrt{E}}{\rho}$.

From the table, based on the performance index $\frac{\sqrt{E}}{\rho}$, Si_3N_4, CFRP and Wood are the most suitable materials.

Table 1: *Values for optimisation function for different materials.*

Material	ρ (Mg m^{-3})	E (GNm^{-2})	$\frac{\sqrt{E}}{\rho}$
Mild Steel	7.8	200	1.81
Stainless Steel	7.8	200	1.81
Al Alloy	2.7	70	3.10
Si_3N_4	3.2	400	6.25
PMMA	1.2	3	1.44
CFRP	1.5	50	4.71
Fibreglass	1.8	20	2.48
Cement	2.5	50	2.83
Wood	0.6	4	3.33

Part *(b)*

A new constraint to the optimisation problem is specified:

$$\begin{aligned} G_c &> 0.5 \text{ kJm}^{-2} \\ \therefore \frac{K_{IC}^2}{E} &> 0.5 \text{ kJm}^{-2} . \end{aligned}$$

Table 2: *Values for toughness constraint for different materials.*

Material	K_{IC} (MN m$^{-3/2}$)	E (GNm^{-2})	$\frac{K_{IC}^2}{E}$
Mild Steel	150	200	112.5
Stainless Steel	150	200	112.5
Al Alloy	30	70	12.9
Si_3N_4	4	400	0.0
PMMA	1	3	0.3
CFRP	10	50	2.0
Fibreglass	20	20	20.0
Cement	1	50	0.0
Wood	2	4	1.0

This new constraint excludes Si_3N_4, PMMA and Cement. CFRP is now the recommended material. Mild steel could potentially corrode in water.

Part *(c)*

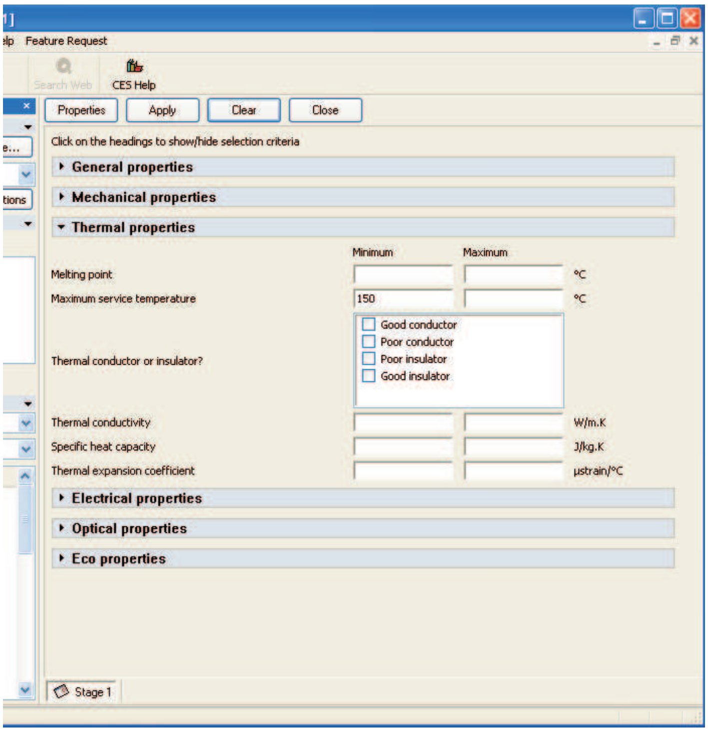
The material must not cost more than 5 per kilogram. This excludes CFRP as a potential choice. Wood is now the best material to make oars out of. Aluminium and fibreglass would also be appropriate.

Question 16

Download the CES Selector from here:
http://www.msm.cam.ac.uk/Teaching/ces/index.html

Create a new project. A tab pops up with three sections. In 2. Selection Stages, click on limit. We want our material to operate at 150 °C, so enter this value into the Thermal Properties > Minimum Service Temperature. This will eliminate around half of the materials. See Figure 6.

Next plot the graph of electrical resistivity against thermal conductivity. Figures 7 and 8 detail how to do this. Figure 9 illustrates the results. It is clear that Aluminium Nitride is the best material available (remember the graph uses logarithmic scales.

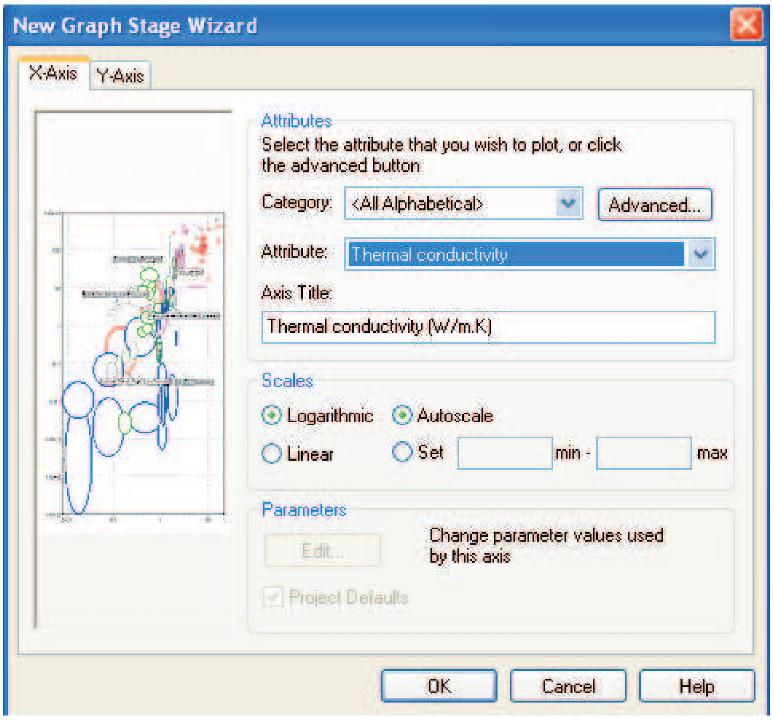


Click on the headings to show/hide selection criteria

	Minimum	Maximum	
Melting point			°C
Maximum service temperature	150		°C
Thermal conductivity			W/m.K
Specific heat capacity			J/kg.K
Thermal expansion coefficient			µstrain/°C

Thermal conductor or insulator?
☐ Good conductor
☐ Poor conductor
☐ Poor insulator
☐ Good insulator

Figure 6: *Stage 1.*



Select the attribute that you wish to plot, or click the advanced button

Category: <All Alphabetical>

Attribute: Thermal conductivity

Axis Title: Thermal conductivity (W/m.K)

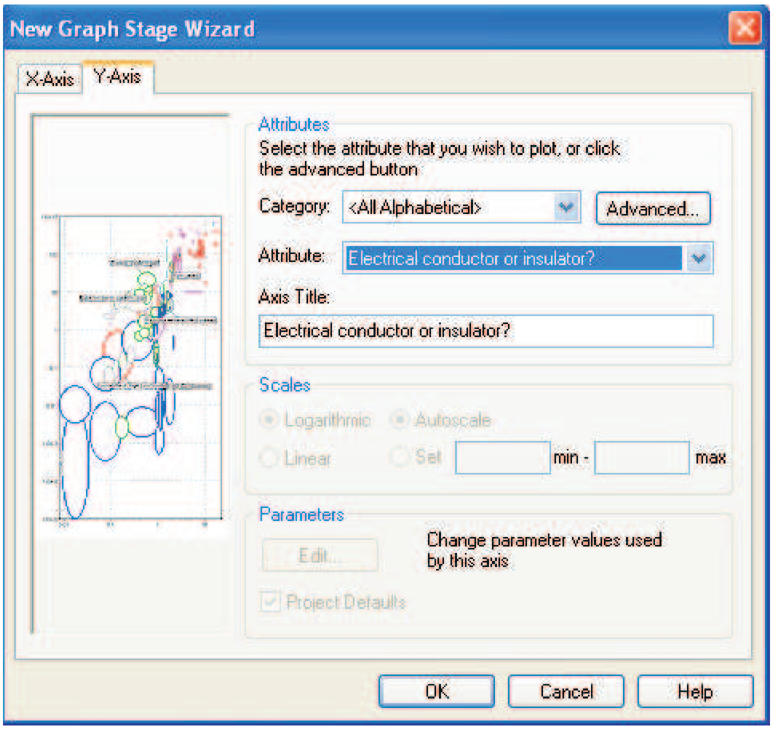
● Logarithmic ● Autoscale

○ Linear ○ Set min - max

Change parameter values used by this axis

☑ Project Defaults

Figure 7: *Stage 2.*



Select the attribute that you wish to plot, or click the advanced button

Category: <All Alphabetical>

Attribute: Electrical conductor or insulator?

Axis Title: Electrical conductor or insulator?

● Logarithmic ● Autoscale

○ Linear ○ Set min - max

Change parameter values used by this axis

☑ Project Defaults

Figure 8: *Stage 2.*

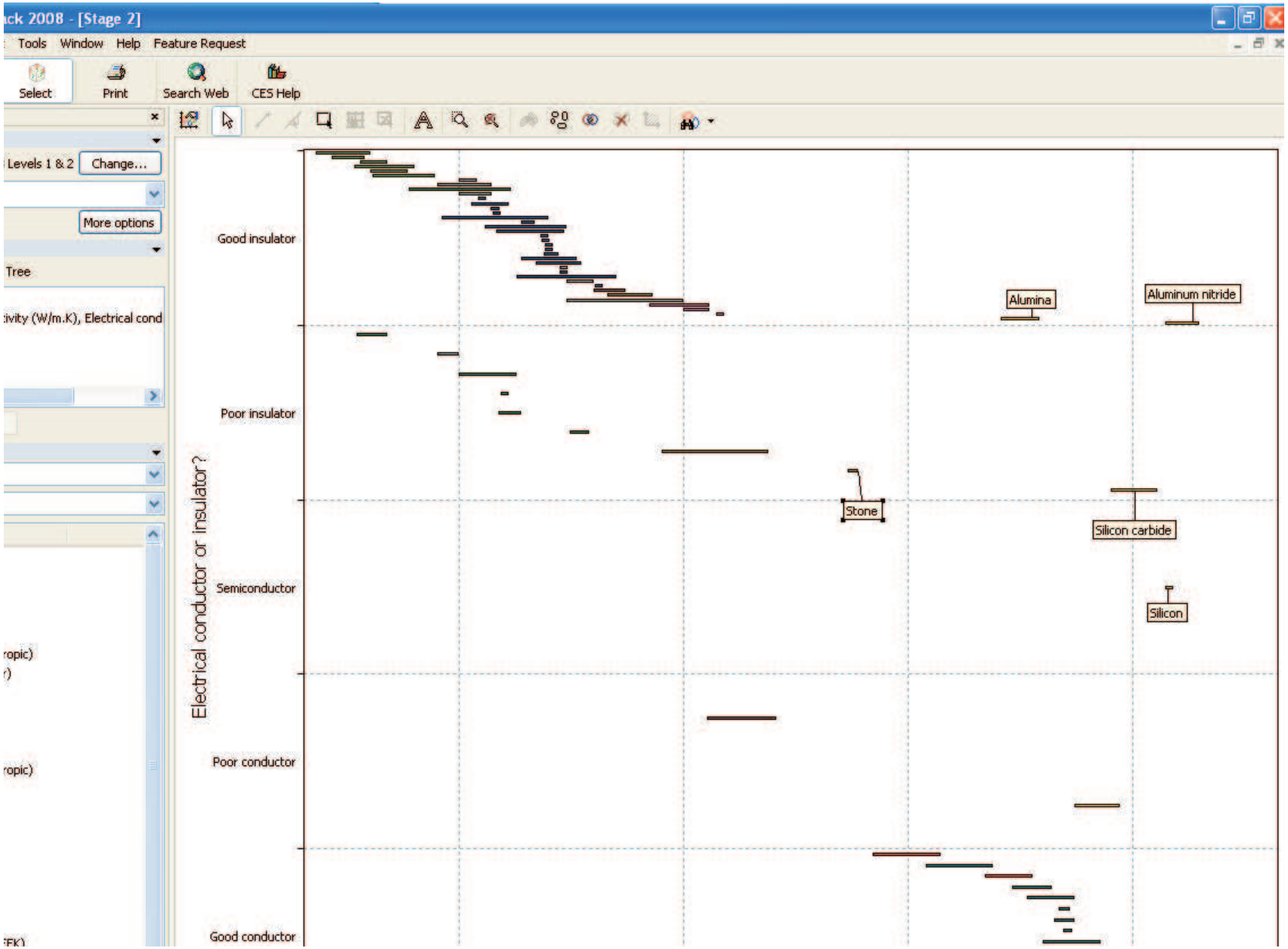


Figure 9: *Resistivity versus Thermal Conductivity.*