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Phenomenological Description of Grain Growth Stagnation for Nanocrystalline Films and Powders

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Abstract. At fixed hold temperatures, grain growth usually stagnates indefinitely after sufficiently long hold times. The change in the growth behavior can be very abrupt, resulting in a sudden plateau in plots of grain size versus time at fixed temperature. Standard grain growth laws do not formally predict the rapid onset of growth stagnation, merely a slow down of grain growth to imperceptible rates. Therefore, the grain size in the plateau regions for long hold times is typically not in agreement with that predicted with kinetic variables derived from the size versus time curves for short hold times where there is pronounced curvature. Standard laws lead to endpoint grain sizes with strong dependences on the hold times. The experimental observation in many cases is a nearly linear temperature dependence that is independent of the hold times after a sufficient duration. Additionally, the growth process may restart from a stagnated state with sufficient temperature increases, where again, the stagnated grain size temperature dependence is linear. For growth laws including size dependent opposing forces, endpoint grain sizes are predicted to be either independent of temperature, or exponentially temperature

dependent with thermodynamic reversibility, the latter an impossibility. We derive, heuristically, a stagnation force, phenomenologically incorporating these observations: a near linear temperature dependence of endpoint grain sizes, and irreversible growth. This description reduces to standard laws commonly used for data fitting, and leads to a normal grain size distribution. Other laws are discussed and compared. Fits to size versus time data are successfully made.

1. Introduction.

For clarity, we must begin by providing reasonable definitions for two types of grain sizes. *Stagnated Grain Size* is grain diameter or radius where there has been a rapid and obvious reduction in the size versus time characteristics at a fixed temperature. Examples of this may be seen in Figs. 6-7. *Endpoint Grain Size* is the grain size reported at a specified time interval in either an experiment or a theoretical prediction.

For nanocrystalline materials, indefinite stagnation of grain growth for fixed hold temperatures and long hold times is frequently observed, Figure 6-7 [1-8]. In thin films, workers have reported that grain growth may be restarted with sufficient temperature increases from an apparently stagnated state, Figure 6 [1-2]. Growth then rapidly restagnates at the new hold temperature. Simple growth laws do not formally predict this rapid onset of stagnation, and therefore, do not predict the correct temperature dependence of endpoint grain sizes from kinetic data extracted before the plateau. In addition, the temperature dependence of stagnated grain sizes is often observed to be nearly linear, and independent of the hold times after a sufficient duration. A near linear temperature dependence on the endpoint grain size is also often reported for experiments with powders [3-8].

Figure 1 shows endpoint grain sizes and stagnated grain sizes for a variety of studies of nanocrystalline materials [1-8]. Note that the endpoint and stagnated grain sizes of all these studies show a near linear dependence on the hold temperature.

Table I shows the stagnated grain size for both normal and abnormal grains from our previous study on abnormal grain growth in Ag, Figure 6 [1]. Note that the abnormal grains stagnate even when their number of sides $N_a > 6$. Figure 1 shows that the slope of the stagnated grain size versus hold temperature is almost the same for abnormal grains and normal grains in our experiments with silver films where the temperature is ramped after stagnation, and for isothermal normal grain growth in Ag films [1-2].

2. Standard Growth Laws.

The simplest growth laws are based on the rigorously derived fact that a surface with surface energy γ and curvature K experiences a driving force toward the center of curvature. The magnitude of this force is $F=\gamma K$. For a perfectly spherical surface of radius r , the curvature $K=1/r$.

A network of multisided grains, in contact with a variety of curvatures, is a many interface problem. Statistically based simplifying assumptions must be made to make a tractable mathematical description of growth behavior. One key assumption is that the net curvature of all the interfaces in the system is given by the inverse of the average grain size, $K_{net}=1/r_{ave}$.

Atoms will traverse the interface by a thermally activated mechanism (typically either surface diffusion or grain boundary diffusion) resulting in an average interfacial velocity v_{ave} proportional to a thermally activated mobility $M(T)$, according to

$$v_{ave} = \gamma M(T)/r_{ave}. \quad (1)$$

Oftentimes, grain growth is observed to fall off with a dependence greater than $1/r_{ave}$. For these cases, it is assumed that there is a size dependent mobility where the size-temperature coupling has the form $M(T)/r_{ave}^{n-1}$. This is not rigorously derivable. This allows for more flexibility in curve fitting, but the resulting classification scheme becomes hard to relate to physical parameters for experimental observations of grain growth where the fall off is faster than the value $n=2$. The interpretation of transport activation energies becomes questionable when $n>2$, and values as high as $n=12$ have been reported [3]. In addition, the use of large constant n values still fail to fit data in the plateau regions.

Equation 1 predicts that in *isothermal-isochronal* annealing experiments (where hold time length and temperature are fixed for each specimen), that the endpoint grain size will have the same temperature dependence as the atomic mobility (typically $\sim e^{-Q/nkT}$). This is the only case in which this law produces any regular temperature dependence on endpoint grain sizes, and why this is the experiment of choice for activation energy extraction. Incorporating the size dependent mobility into Equation 1, the solution is

$$r(T,t)^n = r_o^n + \gamma M(T)t. \quad (2)$$

Since there are no opposing terms to growth, v_{ave} never goes to zero, therefore, there is no formal prediction of a plateau (or r_{ave} constant with time). In addition, there is not even a means to define a *characteristic grain size* or a time length that specifies when the boundary velocity slows down. Therefore, the

endpoint grain sizes predicted by Equation 2 are strongly time dependent, and, the prediction of near linear temperature dependence of endpoint grain size does not follow from this law.

Consider experiments where the temperature is held for a given time interval, raised abruptly to a higher temperature, and held again for another interval, etc. To account for the stagnation and grain growth restart that may be observed in such an experiment, Figure 6, one may try to add an opposing driving force changing monotonically with grain size. For simplicity, consider

$$v_{ave} = \gamma M(T)/r_{ave}^{n-1} - \alpha B(T)r_{ave}^m \quad (3)$$

where α is a constant, $B(T)$ is the mobility of the opposing mechanism assumed to be exponentially dependent on temperature, and m is an exponent like n . $M(T)$ and $B(T)$ have activation energies Q_M and Q_B , respectively. If the opposing force and the force for growth occur via the same transport mechanism, $M(T)=B(T)$, and $v_{ave}=0$ when $r_{ave}=(\gamma/\alpha)^{1/(m+n-1)}$. The equation allows for *formal mathematical* stagnation of the grain growth. However, it predicts that the stagnated grain size is *independent* of temperature. Therefore, under these conditions, the law fails to predict the restart of the growth process from stagnation on temperature increases. An example illustrating this problem is grain boundary pinning by precipitates, often referred to as Zener drag [9].

If the transport mechanisms are not the same in Equation 3, then the stagnated grain size temperature dependence is $r_{ave} = S \exp(-\Delta Q / kT)$, an exponential dependence. The effective "stagnation activation energy" $\Delta Q=(Q_M-$

$Q_B)/(m+n-1)$. If $m+n-1>0$, in order to have a size increase on a temperature increase, $Q_B < Q_M$. This would occur, for example, if the transport mechanism promoting grain growth were grain boundary diffusion. The mechanism opposing grain growth must be controlled by surface diffusion. If $m+n-1<0$ then $Q_B > Q_M$ is required for size increase on temperature increases. In either case, Equation 3 predicts that grain growth should be a *reversible* process, a thermodynamic impossibility. This is illustrated in Figure 2. Such a description would not even be useful for engineering purposes, where it would be desirable to be able to predict endpoint grain sizes under varying process conditions.

Statistical multiplicative factors have been incorporated into Eqns. 1 and 3 to attempt to account for the overall geometry of the grains in the network. One example is the average number of sides of grains in the system, N . When all grains have a geometrically perfect shape, growth should stop, so the growth law is proportional to $(N - N_{perfect})$. For a two dimensional grain, $N_{perfect} = 6$, corresponding to triple junctions where all angles are 120° [10]. However, grain growth has been observed to stagnate well before $N=6$, particularly in the case of abnormal grain growth, where large grains have many more than six sides [1].

3. Phenomenological Description of Stagnation.

The standard growth laws do not account for the near linear temperature dependence of the stagnated grain sizes, and in many cases, endpoint grain sizes. We develop a retarding force to grain growth that does produce linear behavior, and captures the essential features of grain growth restart on temperature increases.

In our work on nanocrystalline Ag, refs. 1-2, it was concluded that thermal grooving impeded grain growth causing stagnation. Abrupt changes in temperature would allow a number of interfaces to escape the thermal grooves, where others could not. We postulated that the internal regions of grain boundaries pinned at the film surface by grooves could migrate such that the boundary angle exceeded the groove angle, and for a short time, move freely until a new groove formed at the surface with sufficient depth to cause stagnation.

With such a mechanism, or any mechanism, not all grains are affected equally. Some boundaries may escape, others may not. Independent of the mechanism, let us consider a statistical weighting function where there is a high probability that any interface can migrate with a sufficient temperature increase, but, will restagnate when its curvature reaches a new, lower value. This probability distribution must result in an *irreversible* growth process, and, a tendency for the network to approach a condition of normal growth. A distribution satisfying these requirements is

$$P(T,r) = 1-\exp(-(AT/r)^Y). \quad (4)$$

A and Y are fitting variables that parameterize the strength of the opposing force and its impact on the network in a general way. Inserted into Equation 1, the new growth law reads

$$v_{ave} = (1-\exp(-(AT/r_{ave})^Y))\gamma M(T)/r_{ave}^{n-1}. \quad (5)$$

The radii resulting from Equation 5 are plotted in Figure 3 for the indicated values of Y and $A=1$. Figure 4 shows the linear dependence of the stagnated grain

size for Equation 5 for sufficiently high values of Y . We have solved numerically for the radii as a function of time from the velocity in Equation 5. We offer no closed form solution for $r(t)$.

The linear characteristic of the stagnated grain size versus temperature can be understood by the $1/e$ value of the exponent, $r_{ave} = AT$. When this condition is met, the average interfacial *velocity* begins to decay rapidly. The irreversibility results from the fact that temperature decreases tend to cause $P(t, T)$ to approach zero. The approach to normal grain size distributions occurs because larger grains are impeded more than smaller ones.

We point out that different starting grain sizes for *normal* growth do not seem to require different A values for good fits. The latter as evidenced by the two Ag normal growth studies shown in Figure 1, where the as deposited film thicknesses were 14 nm and 32 nm respectively in references 1-2 for sputtered Ag films. This is borne out in Equation 5, as it predicts that different starting grains sizes, for the same parameters otherwise, will reach the same final grain size. This probably applies to near fully dense systems, noting reference 5 in Figure 1, an Ag powder study.

Thus far, we have merely introduced a candidate functional form with no underlying physical principles. We can only rationalize our choice of distribution function with a simple analogy. Consider a driving force opposed by a "classical" drag force whose magnitude is proportional to the velocity of the boundary,

$$v = M \cdot F - \alpha_d(r) \cdot M \cdot F. \quad (6)$$

We will suppose that the drag coefficient, $\alpha_d(r)$, changes in size as if the boundary behaves something like a sail, being pushed through a resistive medium at a fixed velocity. The appropriate form must satisfy several conditions.

- 1) Consider the limit of infinite boundary size $r=\infty$. The drag coefficient may not have the simple dependence $\alpha_d = Cr$, since any applied force F would result in motion of the boundary *against* the force. The physically sensible solution is the one which simply prevents any motion, that is, $\alpha_d(\infty)=1$.
- 2) As a second limit, $r=0$ must result in zero drag, so, forms such as $\alpha_d = C/r$ must be excluded.
- 3) Finally, we would like, for some range of grain sizes, to recover the experimentally observed growth law $v \propto 1/r^{p \geq 1}$.

A form for the drag coefficient which satisfies all of these is

$$\alpha_d(r) = \exp(-(C/r)^Y). \tag{7}$$

The requirements on the limits of $r=\infty$ and $r=0$ are satisfied. For $(C/r)^Y \ll 1$, $\alpha_d(r) \approx 1-(C/r)^Y$, which when substituted in Equation 6 results in $v = M \cdot F \cdot (C/r)^Y$ satisfying the third condition, with the relationship between equations 5 and 7 now apparent. C characterizes a systems non-ideality. As $C \rightarrow \infty$ the system is perfectly ideal and there is no opposition to growth.

For a comparison to a standard growth law, if we define a local growth exponent from the standard growth law $v \propto 1/r^{n-1}$ where $n_{loc} = 1 - \partial \ln(v)/\partial \ln(r)$, and

apply this to Equation 5, we essentially have a size dependent n where $n_{loc} = n$ for $r \ll AT$ and $n_{loc} = n + Y$ for $r \gg AT$. The rate of change of the extracted n_{loc} with r depends on A and Y , Figure 5 and Equation 8. So, although this law also does not predict stagnation of growth in a formal manner, it does provide for a very abrupt increase in n , which in a short time experiment, would appear as a rapid onset of stagnation. It would also explain why exponents extracted for short duration experiments result often in $n=2-3$, but points in the plateau regions must be ignored in order to produce these results, and, why including points in the plateau tends to drive n up. Thus, assuming $C=AT$, the local growth exponent expressed in its complete form is

$$n_{loc} = n + Y(AT/r)^Y \exp(-(AT/r)^Y) (1 - \exp(-(AT/r)^Y))^{-1}. \quad (8)$$

4. Analysis.

Figure 6 shows the fit of Equation 5 to our abnormal grain size data for Ag films, from reference 1. The parameter set is given in Table II. The $Q=0.274$ eV is taken from our estimate in reference 1, where the growth exponent $n=2$ was assumed in the analysis. Only slightly different A values were used when greater or less than $T=300^\circ\text{C}$, but the other parameters were constant. Note the large value of Y necessary to fit the data of reference 1.

Figure 7 shows our fit to the data of reference 3 using Equation 5, a study of nanocrystalline iron. We have fit the full range of the annealing time with Equation 5, using $n=2$, $Q=0.49$ eV, although a sharp change in Y and A were necessary between $725-825$ K. Two separate regions of behavior can also be seen in Figure 7.

The parameter sets used are shown in Table 3. It can be noted that the data set of 805 K can be fit very well (shown as the dotted line in Figure 6) with the exception of one point. The fit at 805 K combines the Y values of the lower temperatures with the A values of the higher temperatures, but a different γM_o was necessary, and we will treat this data set as an exception. The activation energy $Q=0.49$ eV was chosen so that γM_o would be nearly temperature independent for the data sets, other than 805 K.

5. Discussion.

This analysis shows it is possible to use a standard growth law for short times after temperature changes with $n=2$ and a single activation energy with a nearly constant mobility pre-exponential. Since $n=2$ for short hold times, the Q can be physically interpreted: since $Q<0.5$ eV for the cases in refs. 1 and 3, grain growth is controlled by surface diffusion. Essentially the same parameter set can also fit the data over a long range of hold times into the plateau, and over a range of temperatures. A single transport mechanism is assumed to be in operation. The long duration pinning force increases sharply with temperature via A and Y , Table II. The rapid rise of the pinning force with grain size, using the law given by Equation 5, allows the long-term behavior to be de-coupled from the short-term behavior, while all variables influence the intermediate behavior. Large n values and potentially unphysical activation energies in the early growth stage need not be used to compensate for the long term behavior. In addition, this law allows for the restart of the growth process from hard stagnation on temperature increases with virtually the same parameter set, Figure 6.

Important physical questions that remain to be addressed are:

- 1) On what are the boundaries dragging ?
- 2) What is responsible for the relation $C=AT$?

Some theoretical work has been done on drag forces due to triple junctions in thin film grain boundary networks, but whether the two ideas can be connected is unclear [11].

One may speculate that the drag force is indirectly connected with the grain size by some known mechanism. For example, grain boundary impurity or precipitate density increases as grain size increases, creating a drag force increasing with grain size. For films, grains grow with time, and thermal grooves deepen. Boundaries pinned at the surface by deepening thermal grooves (for the same groove angle) take longer to develop the greater internal curvatures to needed escape them, causing a decrease of average boundary velocity. One may imagine many possible combined mechanisms. For the engineer who wishes to characterize his system predictively and is unable to deconvolute the effects of multiple mechanisms , this law could be useful.

Still, the stagnation behavior seems to be quite general. The same late stage growth behavior occurs for a variety of materials, whether films or powders, metals, or dielectrics. This behavior may very well be a late growth stage effect, inherent in any system, unaccounted for by theory or in the common methods of analysis.

For example, consider the total interfacial energy of a grain boundary network, as a function of the grain size. As the average grain size increases and the total system energy approaches a global minimum, perhaps the total system energy may have an increasing density of local minima. Energy input (temperature increase) is required to jog the system out of a local minima, and grain growth proceeds until the next local minima is encountered, etc. The system would like to reach the ultimate state of perfection, which is the elimination of all interfacial energy resulting in a single crystal with no grain boundaries (zero misorientation for all “boundaries”). The next best thing to a single crystal is for the system to develop a dense concentration of coincidence-site-lattice boundaries (CSL). CSL boundaries are known to result in deep minima or “cusps” in the surface energy as a function of misorientation. The system “drags” on its own perfection. The evolution of the system as a whole cannot be captured by simple growth laws which only generalize the behavior of a single curved surface, and ignore detailed interfacial interactions.

6. Conclusions

Standard growth laws fail to predict the temperature dependence of stagnated or endpoint grain sizes in film or powder nanocrystalline systems, often experimentally observed to be linear. Traditional explanations for stagnation, such as film thickness effects or opposing forces, fail to explain the restart of growth from stagnation with thermodynamic irreversibility.

A size dependent drag force proportional to the velocity of the boundary with a drag coefficient $\alpha_d(r) = \exp(-(C/r)^Y)$ is proposed. This form satisfies size limits,

thermodynamic irreversibility, the approach to normal grain size distributions, and reduces to a common growth law where $v \propto 1/t^{p \geq 1}$. It has been fit to experimental data for short-term growth and for long-term growth in the plateau with reasonable precision, allowing one transport mechanism to be used for the data investigated. It has been possible to use the rigorously derivable growth exponent $n=2$ in all cases examined. If $C=AT$, then the law allows for a restart of the growth process from stagnation, a near linear final size dependence on temperature with a single parameter set, and a characteristic grain size for slow growth at a given temperature $r_{char} = AT$.

Theoretical work is needed to relate the proposed form of the opposing force to physical mechanisms. Denser time vs. grain size data than what was used in the present work, taken over long hold times, will be required to attempt simultaneous fits of the short term and long term grain sizes, with the single parameter set $(Y, A, Q, n, \gamma M_0)$.

The often experimentally reported stagnated and endpoint grain size is linearly temperature dependent. This results whether the specimens are films or powders, and the behavior may prove to be very general. Perhaps this phenomenological description may initially be used as a classification scheme where it is found that A and Y show material dependences. Engineers may find this law useful for characterization of materials and to accurately predict endpoint grain sizes for varying process conditions.

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References

1. Rand Dannenberg, Joanna Groza, Eric Stach, Brian Dresser, *Thin Solid Films* 370 (2000) 54-62.
2. Rand Dannenberg, Joanna Groza, Eric Stach, Brian Dresser, *In-Situ TEM Study of Normal Grain Growth in Silver Thin Films*, in submission to *Thin Solid Films* (2000).
3. T.R. Malow, C.C. Koch, *Acta mater.* 45 5 (1997) 2177-2186.
4. L.Z. Zhou, J.T. Guo, *Scripta Materialia*, 40 2 (1999) 139-144.
5. Tokushi Kizuka, Hideki Ichinose, Yoichi Ishida, *J. of Mat. Sci.* 32 (1997) 1501-1507.
6. H.G. Kim, K.T. Kim, *Acta mater.* 47 13 (1999) 3561-3570.
7. A. Sturm, U. Betz, C. Scipione, H. Hahn, *Nanostructured Materials* 11 5 (1999) 651-661.
8. J.L. Shi, *J. Mater. Res.* 14 4 (1999) 1389-1397.
9. C.S. Smith, *Trans. AIME* 175:15 (1948).
10. J. Von Neumann, *Metal Interfaces*, ASM (1952) 108.
11. Alexander H. King, private communication.

Tables.

Table I. Stagnated abnormal grain size data for 80 nm thick Ag films [1].

^a calculated from the average value of the plateau.

<i>Time (mins)</i>	<i>Temp (C)</i>	<i>D_a (nm)^a</i>	<i>D_n (nm)</i>	<i>N_a</i>
121	100	159	26	19.2
181	200	206	74	8.75
201	300	223	84	8.37
208.5	350	242	90	8.4

Table II. Fit parameters for Equation 5 to our abnormal grain size data for Ag films [1]. The fit is shown in Figure 6.

	Y	A (nm/K)	Q (eV)	n	γM_0 (nm ² /s)
$T < 300^\circ\text{C}$	110	0.205	0.274	2	$1.3 \cdot 10^4$
$T > 300^\circ\text{C}$	110	0.185	0.274	2	$1.3 \cdot 10^4$

Table III. Parameters used for the fits in Figure 7, reference 3. $Q=0.49$ eV and $n=2$. The bold emphasizes the "hybrid" nature of the 805 K data set.

	Y	A (nm/K)	γM_o (nm ² /K)
875 K	60	0.034	25
825 K	60	0.032	25
805 K	<u>20</u>	<u>0.030</u>	<u>14</u>
725 K	20	0.0113	23
675 K	20	0.01	25
625 K	20	0.01	25

Figure Captions.

Figure 1. Stagnated and endpoint grain sizes for a variety of thin film and powder studies. Normal and abnormal grain sizes in thin films of Ag are from references 1-2. The slopes of these lines for the normal and abnormal grains is 0.31 and 0.24 nm/K, respectively. Note that the slopes of the curves from the references 1-2 are nearly the same. Reference 2 is an isothermal annealing study, and reference 1 is a study where the temperature is ramped after obvious stagnation. The remainder of the references are for isochronal-isothermal annealing studies.

Figure 2. Growth according to Equation 3 with $n=2$ and $m=1$ for temperatures of 400 K – 550 K in 50 K increments and hold times of 3000 time units. The last hold temperature is a reduction from 550 K to 500 K. Equation 3 unfortunately predicts a reversible growth process. $Q_M = 1$ eV and $Q_B = 0.3$ eV .

Figure 3. Equation 5 plotted for 400-800 K in 100 K increments, with $A=1$ nm/K and the indicated Y . $Q=1$ eV and $n=2$.

Figure 4. Note that the stagnated grain size is linearly dependent on temperature for a growth law such as Equation 5, when Y becomes sufficiently large.

Figure 5. Local mode parameter n_{loc} for $n=2$, $Y=5$ and 10 , $T=300$ °C.

Figure 6. Fit of equation 5 to our abnormal grain size for Ag films, from reference 1, with parameters in Table 2. The plateaus correspond to temperatures of 100°C, 200°C, 300°C, 350°C.

Figure 7. Fits of equation 5 to the data of reference 3, a study of nanocrystalline Fe. The corresponding parameter sets are shown in Table 3.

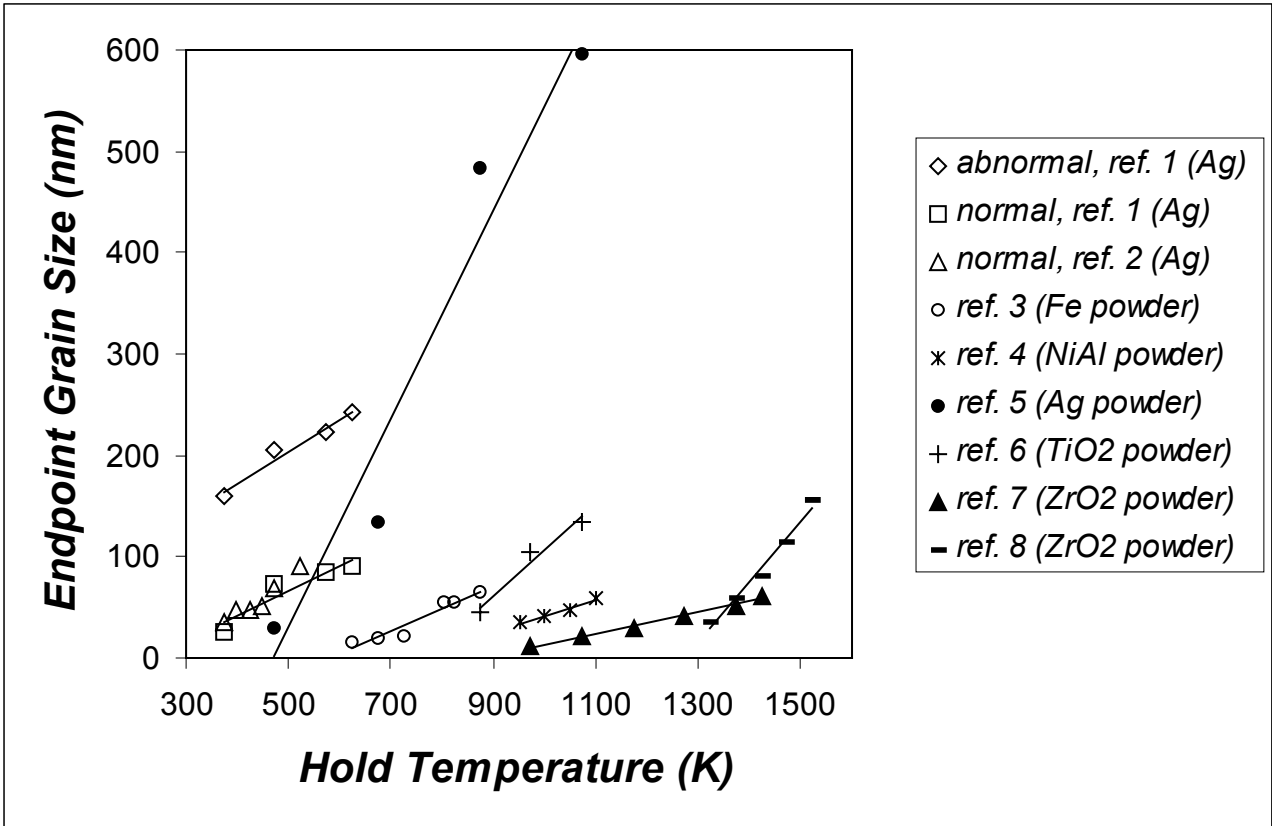


Figure 1.

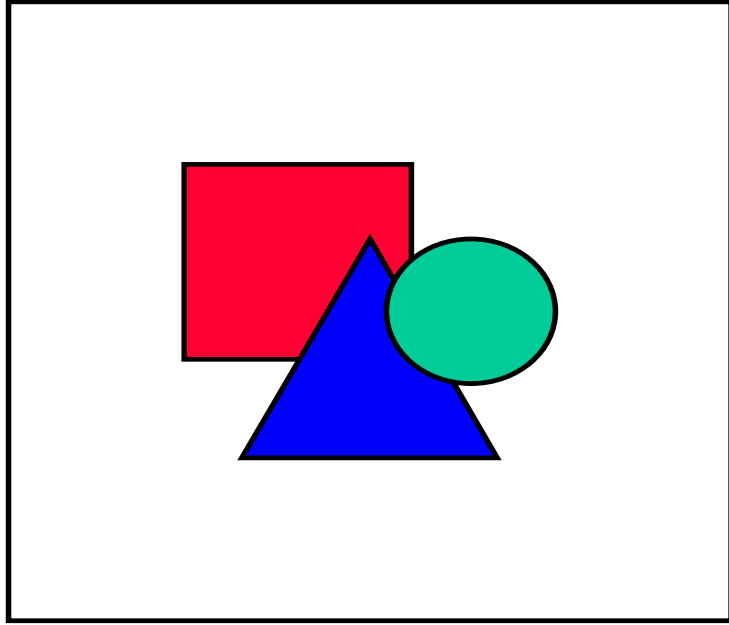


Figure 2.

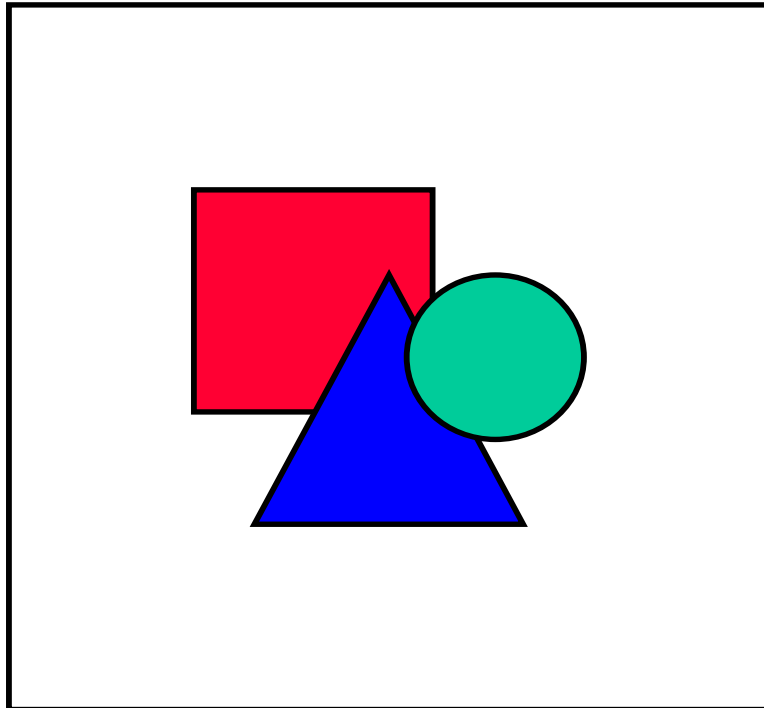


Figure 3.

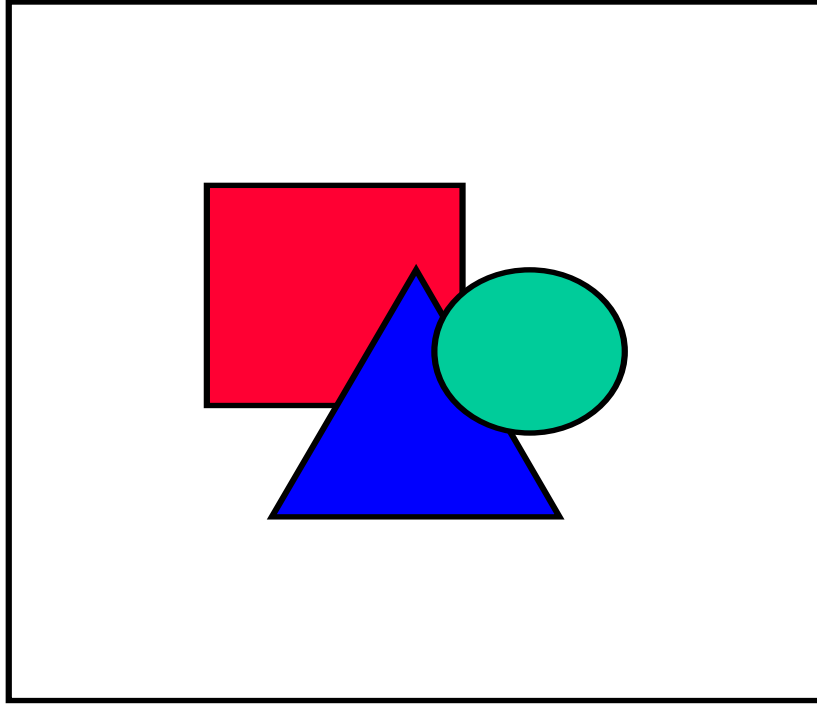


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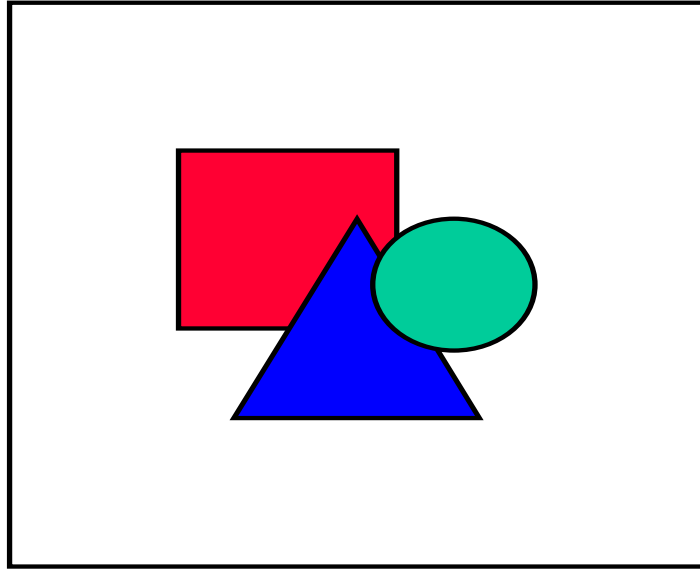


Figure 5.

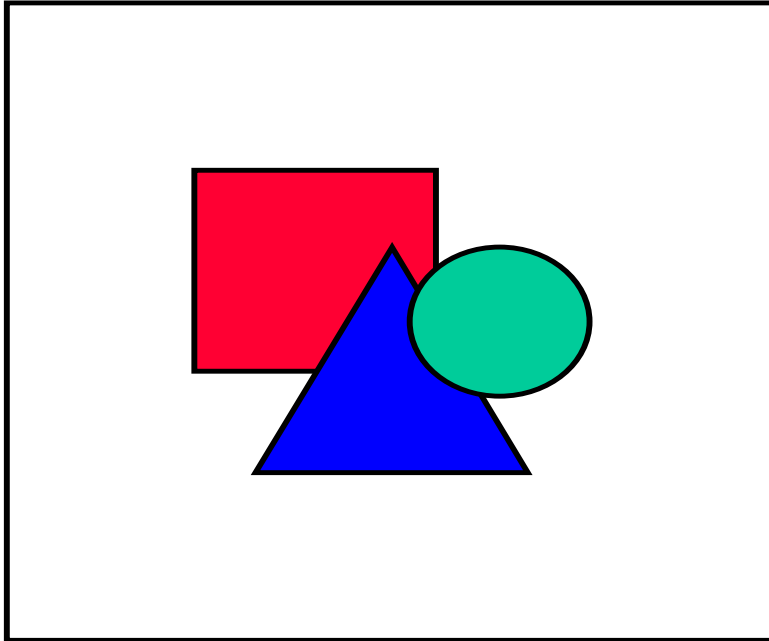


Figure 6.

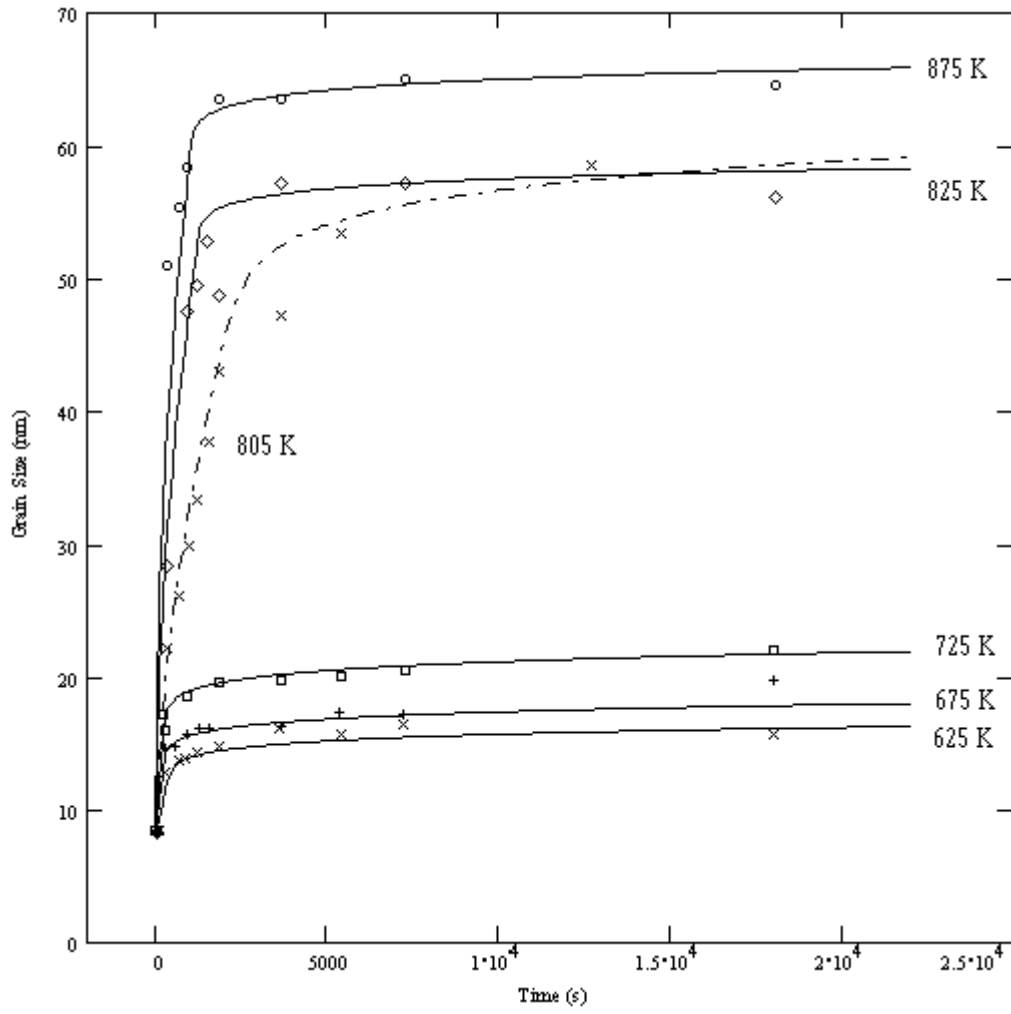


Figure 7.