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The mechanical properties of some nickel-copper and nickel-copper-carbon alloys below 0.35 T[subscript m]

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THE MECHANICAL PROPERTIES OF SOME NICKEL-COPPER
AND NICKEL-COPPER-CARBON ALLOYS BELOW 0.35 T_m

by

Robert Paul Zerwekh

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Iowa State University
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1970
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I. INTRODUCTION

Nickel and copper form a continuous series of solid solutions over the entire range of compositions from pure nickel to pure copper, although recent work has indicated that a tendency toward clustering might exist near the equiatomic composition (1). The nickel-copper phase diagram is given in Figure 1 (2).

Besides pure nickel and copper, important alloys in the system are nickel-30% copper (Monel) and copper-30% nickel (Cupro-Nickel). Monel is useful in applications where contact is made with corrosive environments, e.g., acids and seawater. Typical uses for Cupro-Nickel are in condensers and as evaporator and heat-exchanger tubes. The literature is abundant with engineering data on these two alloys and their variations.

Fundamental mechanical property studies have been done on nickel and copper, but very little work of this nature has been carried out on the nickel-copper system per se. Osswald (3) looked at the single crystal deformation of nickel-copper single crystals at room temperature. Recently, Blakemore and Hall (4) and Blakemore (5) extensively explored the phenomenon of serrated flow in nickel-copper-hydrogen and nickel-copper-carbon alloys. Their results will be discussed in some detail in the next section.

The thermodynamics of deformation have been studied in
Figure 1. The nickel-copper phase diagram (2)
many pure metals, mostly body-centered cubic (6), but some face-centered cubic metals have been worked on, nickel (7, 8) and copper (9) among them. However, these kinds of experiments have not been done on nickel-copper alloys. In addition, a systematic study of the effects of substitutional alloying on 1) the activation energy for dislocation glide, 2) the activation volume, and 3) the effective shear stress has to date not been done in any substitutional system. Nickel-copper lends itself to this kind of program because several quantities change in a regular way across the range of compositions. The lattice parameters increase slightly from 3.5236Å for nickel to 3.6145Å for copper (10). The stacking fault energy decreases from an estimated 400 ergs/cm² to about 150 ergs/cm² in the mid-composition range (11). The elastic constants decrease linearly with copper content (12). Finally, the transition character of the system decreases due to 3d-shell filling as copper is added (13). All of these might have some effect on the observed deformation characteristics. Accordingly, one objective of this research was to ascertain which parameter has the greater effect on the rate controlling dislocation mechanisms operating during deformation.

The influence of interstitial impurities on the mechanical properties of body-centered cubic metals is rather well defined. However, in face-centered cubic structures there is little information, with the exception of nickel (8) and
thorium (14, 15). The reason is that the solubility of interstitials, notably carbon, is generally low in face-centered cubics. Thorium is an exception, having a very high solubility for carbon even at room temperature (16). In nickel, the carbon solubility is rather high at elevated temperatures, but drops rapidly toward zero at room temperature. This is shown in the nickel-carbon phase diagram, Figure 2 (17). As a result, in mechanical property studies of the nickel-carbon system, rapid quenching has been a necessity, producing non-equilibrium alloys (8, 18).

Another aspect of this work then is to evaluate how the mechanical properties, as affected by a given amount of carbon, are altered in the nickel-copper system as the copper content is varied. As noted, this aspect with respect to serrated flow is well known but there are virtually no data regarding other mechanical properties, especially dislocation dynamics. In particular, therefore, the objective is to discover what role carbon plays in the dislocation mechanisms associated with plastic deformation in nickel-copper-carbon alloys, and if this role changes as the character of the host matrix (nickel-copper) changes.
Figure 2. The nickel-carbon phase diagram (17)
II. LITERATURE SURVEY

A. Mechanical Properties of Nickel-Copper and Nickel-Copper-Carbon Alloys

The mechanical properties of pure nickel are well documented for both single and polycrystals (7, 8). There are, however, relatively little data concerning the influence of impurities on the mechanical properties of nickel. Pure nickel exhibits typical "face-centered cubic" behavior with respect to flow stress-temperature. That is, the flow stress is relatively insensitive to temperature and increases very little as the temperature is decreased. Flinn (18), however, found a strong effect due to carbon, especially at low temperatures. He rapidly quenched tensile specimens containing 0.5 and 1.0 atomic percent (a/o) carbon from high temperatures where the carbon was in solution. The solubility as a function of temperature is shown in Table 1 (19). These non-equilibrium solid solutions showed a dramatic increase in strength when the temperature was lowered. For instance, the proportional limit of the alloy containing 0.5 a/o increased from about 7 Kg/mm\(^2\) at 373°K to about 27 Kg/mm\(^2\) at 4.2°K, nearly a four-fold increase. Flinn attributed this to a Cottrell locking mechanism in nickel.\(^1\)

\(^1\)"Cottrell locking" implies a mechanism whereby atmospheres of interstitial solute atoms surround the glide dislocations, thus exerting a drag force on them.
Table 1. Temperature dependence of carbon solubility in nickel

<table>
<thead>
<tr>
<th>Carbon Solubility</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>Atomic %</td>
</tr>
<tr>
<td>--------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>0.5</td>
<td>2.4</td>
</tr>
<tr>
<td>0.4</td>
<td>1.95</td>
</tr>
<tr>
<td>0.3</td>
<td>1.45</td>
</tr>
<tr>
<td>0.2</td>
<td>0.95</td>
</tr>
<tr>
<td>0.1</td>
<td>0.48</td>
</tr>
<tr>
<td>0.08</td>
<td>0.40</td>
</tr>
</tbody>
</table>

aSolubility can be expressed; ln wt. % = 2.480-4880/T°K. This relation is taken from the work of Lander et al. (19).

purities not only raise the critical resolved shear stress, they also tend to increase the extent of easy glide. Latanision and Staehle (20) found that in 99.98 purity nickel (nickel "270") the easy glide region was finished at 5 to 7 percent strain. In lower purity material, 99.8%, easy glide was present out to 40 percent. Haasen (7) found similar results. No explanation has been given for this phenomenon.

Recently, some of the most complete work on nickel and nickel-carbon alloys has been done by Sonon and Smith (8). Their work also included a study of nickel-cobalt and nickel-cobalt-carbon alloys. They found that increasing the carbon content increased the strength of both nickel and nickel
alloys containing 60 weight percent (w/o) cobalt, especially at low temperatures. The 0.2% offset yield stress depended linearly on carbon content in nickel, and on the square root of carbon content in Ni-60 w/o Co. In nickel, strengthening was attributed to pairs, or possibly even larger clusters, of carbon atoms which could cause unsymmetrical distortions. These would be necessary to explain the observed rate of strengthening. This proposition is supported by the internal friction work of Kê and Chang (21), and later experiments performed by Diamond and Wert (22). Strengthening in Ni-60 w/o Co was attributed to carbon pairs or clusters, but complications prevented a complete analysis.

Sonan and Smith observed serrated flow in nickel containing 0.081 weight percent carbon in the temperature range between 275° to 525°K at a strain rate of 8.34x10^-5 sec^-1. Additions of cobalt moved the range to a much higher temperature. In Ni-60 w/o Co-.059 w/o C serrations were seen between 500° and 600°K.

The rate of increase of flow stress with decreasing temperature, from 300° down to 78°K, seemed to be about the same for nickel and Ni-60 w/o Co, except perhaps at the lower carbon levels. Nickel with .002 w/o carbon exhibited very little temperature dependence, whereas Ni-60 w/o Co with .007 w/o carbon showed a definite dependence. At 6% offset strain, the temperature dependence of the flow stress was increased for the low carbon nickel, and stayed about the same
for the nickel-cobalt alloy. This finding is in basic agreement with that of Geil and Carwile (23), who found that the proportional limit of pure nickel was about constant between 373° and 78°K. However, at higher strains, a clear temperature dependence developed. These same kinds of trends have been found in nickel single crystals. Haasen (7) reported an average critical resolved shear stress of about .65 Kg/mm² at 300°K. At 78°K it was .80 Kg/mm². At the onset of rapid work hardening, i.e., the beginning of stage II, the flow stress was 0.95 Kg/mm² at 300°K. At 78°K it had increased to 1.6 Kg/mm². Very recent work by Venkatesan and Beshers (24) tends to confirm Haasen's data. However, their crystals were of higher purity, being zone refined and beam melted. The critical resolved shear stress between 77° and 298°K decreased from .65 to .63 Kg/mm², indicating essentially no temperature dependence. The flow stress at the onset of stage II decreased from 1.24 to 0.82 Kg/mm².

Blakemore has studied the effects of hydrogen (4) and carbon (5) on the serrated flow of nickel and various nickel alloys. He found in nickel-hydrogen that the temperature range where serrated flow could be observed was between -130° and -40°C. Additions of copper narrowed this range until at 50 w/o Cu the serrations disappeared. Static strain aging tests gave about the same temperature range for the presence of an upper yield point, but it disappeared at 60 w/o Cu.
Blakemore attributed this narrowing of the temperature range to a combination of lowered solute diffusion rate and lowered binding energy of the solute with dislocations, plus the factor of increasing yield stress due to solid solution strengthening.

When the interstitial element was carbon, different behavior was noted. Blakemore found the temperature range for visible serrated flow to be narrowed, but also shifted upward. The carbon level in these alloys was about 0.020 w/o. Blakemore used a strain rate of $1.37 \times 10^{-4}$ sec$^{-1}$. In this study the effects of cobalt additions were also evaluated. The main results of Blakemore's work are summarized in Figure 3.

Serrated flow in nickel was attributed by Blakemore to carbide precipitation because the upper temperature where the phenomenon vanished agreed with the temperature for carbide decomposition.\(^1\) An increase in this temperature with copper additions was thought to be due to a shift in the phase boundary. Effects due to electronic and local order interactions, as well as Suzuki locking, were thought not to be important with regard to serrated flow in nickel-carbon and nickel-copper-carbon alloys.

\(^1\)This conclusion by Blakemore will be examined in some detail in Appendix A.
Figure 3. The temperature range for the Portevin-Le Chatelier effect in carburized nickel-copper and nickel-cobalt alloys (5)
B. Thermally Activated Deformation

Plastic deformation in crystalline solids occurs primarily by the motion of lattice defects called dislocations. In addition, the plastic deformation of metals is now generally regarded as being, at least partially, a thermally activated or rate phenomenon (25, 26, 27) which is reflected in the variation of flow stress with strain rate and temperature. Accordingly, since plastic deformation can be a rate phenomenon, it follows that the motion of dislocations can be a thermally activated process. That is, thermal fluctuations can aid the dislocations in surmounting local obstacles which may impede their motion through the lattice. The tensile strain rate can thus be described by an equation of the following form (27),

\[ \dot{\epsilon} = N A b v \exp\left[\frac{-\Delta G}{kT}\right] \]  

(1)

In this expression, \( N \) is the number of points per unit volume where glide dislocations are held up by local obstacles, \( A \) is the area swept out by a dislocation segment when an obstacle is surmounted, \( b \) is the Burgers vector, and \( v \) is the vibrational or "attempt" frequency of the segment when a successful activation event has occurred. In general, the quantity \( N A b v \) is assumed constant. Equation (1) then becomes
\[ \dot{\varepsilon} = \dot{\varepsilon}_0 \exp[-\Delta G/kT] \]  

(2)

The pre-exponential \( \dot{\varepsilon}_0 \) is called a "structure factor." When it is taken to be a constant, as is usually the case, the thermodynamic treatment of plastic flow is greatly simplified.

Thermal fluctuations can aid dislocations in surmounting only certain kinds of barriers which are termed "short-range" or "local" obstacles. Such obstacles possess stress fields of \( 10b \) (10 Burgers vectors) or less. Examples of short-range obstacles are the Peierls-Nabarro stress, random dispersions of interstitial solutes, forest dislocations, and cross-slip. As the temperature is increased, the amount of stress required to overcome obstacles of this type decreases. Theoretically a temperature is reached where the short-range obstacles are effectively transparent and no longer present any resistance to plastic flow. Further temperature increases should then cause no significant change in the flow stress. This is the temperature independent region of plastic flow.

That part of the flow stress which is temperature independent is called the athermal component. It varies with temperature only as the shear modulus \( \mu \) of the material. The athermal component represents obstacles to dislocation motion that are too large to be overcome by thermal fluctuations. These barriers have stress fields that are significantly greater than \( 10b \), and are called "long-range" obstacles. Common
athermal barriers are other dislocations on parallel glide planes and large incoherent second phase particles.

The flow stress of a metal then is considered to be composed of two distinct parts, the thermal and athermal components. The thermal component $\tau^*$ is a function of temperature and strain rate, and the athermal component $\tau_\mu$ varies with temperature only as the elastic constants are influenced by temperature. As a result, the flow stress $\tau$ of a crystalline material can be expressed (25),

$$\tau = \tau^*(T, \dot{\gamma}) + \tau_\mu .$$

If Equation (1) is a valid representation, then $\tau$ as a function of temperature should be similar to the schematic diagram (25) in Figure 4. This is, in fact, the case. Many metals do exhibit precisely such behavior. The quantity of interest, of course, is $\tau^*(T, \dot{\gamma})$ because it is representative of the rate properties of plastic flow, i.e., the operative barriers to dislocation glide.

When the movement of a dislocation is aided by thermal activation, a volume is swept out which is

$$v = bdl .$$

In this relation, $l$ is the length of dislocation segment involved, $b$ is its Burgers vector, and $d$ is the distance the segment moves to attain the saddle-point configuration. The
Figure 4. Temperature and strain rate variation of the flow stress showing thermal and athermal components (25)
volume \( v \) is then called the "activation volume." The activation volume is defined such that \( v \tau \) represents the total work done on the system by an applied shear stress \( \tau \) during an activation event. Further, when the condition of constant structure applies, the activation volume is

\[
v = kT \left( \frac{\partial \ln \dot{\varepsilon}}{\partial \tau} \right)_{T, \dot{\varepsilon}_0} = -\left( \frac{\partial \Delta G}{\partial \tau} \right)_{T, \dot{\varepsilon}_0}.
\]

(5)

It is apparent that \( v \) can be readily determined from experimental measurements, notably the stress dependence of the strain rate. The activation volume is thus very easily determined from instantaneous strain rate change tests. It is an important quantity because each rate-controlling dislocation mechanism in the deformation process has a characteristic activation volume. Typical values, in terms of \( b^3 \) are listed below (25).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Activation Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overcoming Peierls-Nabarro stress</td>
<td>( 10^2 - 10^3 b^3 )</td>
</tr>
<tr>
<td>Intersection of dislocations</td>
<td>( 10^2 - 10^4 b^3 )</td>
</tr>
<tr>
<td>Nonconservative motion of jogs</td>
<td>( 10^2 - 10^4 b^3 )</td>
</tr>
<tr>
<td>Cross-slip</td>
<td>( 10^1 - 10^2 b^3 )</td>
</tr>
<tr>
<td>Climb</td>
<td>( 1 b^3 )</td>
</tr>
<tr>
<td>Interaction with random solutes</td>
<td>( 10^1 - 10^2 b^3 )</td>
</tr>
</tbody>
</table>

The activation energy \( \Delta G \) is that energy required for a dislocation segment to move from an equilibrium position
to a saddle-point so that it can subsequently move a comparatively large distance. It is given by (26)

\[ \Delta G = \frac{Q + T \frac{\partial u}{\partial T} \frac{T}{\mu} v}{1 - \frac{T}{\mu} \frac{\partial u}{\partial T}} \]  \hspace{1cm} (6)

\( Q \) is the "experimental" activation energy for the movement of a dislocation and represents the \( \Delta H \) for the process. Accordingly, it is defined as (26)

\[ Q = kT^2 \left( \frac{\partial \ln \dot{\varepsilon}}{\partial T} \right)_0 = \Delta G - T \left( \frac{\partial \Delta G}{\partial T} \right)_\tau = \Delta H. \]  \hspace{1cm} (7)

If \( \dot{\varepsilon} \) is taken to be a function of temperature and applied shear stress only, then \( Q \) can be written

\[ Q = -T \left( \frac{\partial T}{\partial T} \frac{\partial \Delta G}{\partial \dot{\varepsilon}} \right) \dot{\varepsilon} \]  \hspace{1cm} (8)

by virtue of the chain rule. Inserting (8) into the expression for the Gibbs free energy \( \Delta G \), and by appropriate rearrangement of terms, we have

\[ \Delta G = -kT^2 \frac{\partial \ln \dot{\varepsilon}}{\partial \ln 
\dot{\varepsilon}} \dot{\varepsilon}_0 \left[ \frac{\partial \ln \sigma}{\partial T} \dot{\varepsilon}_0 \right] - \frac{\partial \ln \nu}{\partial T} \frac{1}{1 - T \frac{\partial \ln \nu}{\partial T}}. \]  \hspace{1cm} (9)

In this equation, the use of the applied tensile stress \( \sigma \) and tensile strain rate \( \dot{\varepsilon} \) is permissible because the logarithms of ratios are used rather than of absolute quantities. As a result, conversions to shear stress and shear strain rate are not necessary. The shear modulus \( \mu \) is defined as

\[ \mu = \frac{1}{3} (C_{11} - C_{12} + C_{44}) \]  \hspace{1cm} (10)
It is clear, therefore, that \( \mu \) can be readily determined from measurements of second-order elastic constants. Fortunately, this information is generally available in the literature (12, 28, 29). The term \( (\partial n_e / \partial n_\sigma) \) is obtained from instantaneous strain rate change tests.

Some discussion of \( (\partial n_\sigma / \partial T) \) is required because to be rigorously correct it should be determined from instantaneous temperature change tests so that the requirement of constant structure is fulfilled. However, this is experimentally very difficult to accomplish due to the time required to switch temperature baths and then have thermal equilibrium established between the specimen, grips, and tensile cage. Further, as soon as loading is stopped prior to a temperature change, relaxation processes begin, indicating a change in structure. This problem has been recognized by several workers (8, 14, 30). In order to obtain more reliable and consistent values of \( (\partial n_\sigma / \partial T) \) the instantaneous slopes of the flow stress vs. temperature curves have been used in recent work with good success (8, 14).

As with the activation volume, the activation energy can also be used to discriminate between rate-controlling dislocation mechanisms, each mechanism having a characteristic \( \Delta G \). In actual practice, however, the activation volume is probably more reliable and informative because fewer experimental quantities are required for its determination and it reflects
the physical characteristics of the deformation controlling process.

When evaluating activation volume and energy, it is perhaps more useful to consider how they vary with the effective shear stress \( \tau^* \) rather than the applied shear stress. The effective stress, as noted earlier, is the thermal component of the flow stress. Experimentally it can be determined from the flow stress vs. temperature curves, and is expressed as

\[
\tau^* = \tau - \tau_\mu = \frac{\sigma - \sigma_\mu}{3.06} = \frac{\sigma^*}{3.06} .
\]  

(11)

The temperature independent portion of the flow stress is \( \sigma_\mu \), and 3.06 is the Taylor averaging factor (31) for finding the shear stress in face-centered cubic polycrystals.

At this point, a more complete discussion of some of the short range obstacles outlined on page 16 would be of benefit.

The critical shear stress for a dislocation to overcome the intrinsic "lattice friction" of a material is (32)

\[
\tau = \frac{2\mu}{(1-\nu)} \exp[-2\pi a_0/b(1-\nu)] .
\]

(12)

This quantity represents the so-called Peierls-Nabarro stress. In the expression, \( \mu \) is the shear modulus, \( \nu \) is Poisson's ratio, \( a_0 \) is the lattice spacing, and \( b \) is the Burgers vector. Calculations show that \( \tau \) is greater for body-centered cubic metals than for face-centered cubic metals. At low
temperatures in face-centered cubic metals, the Peierls-Nabarro stress was considered to be so small that it could not be one of the rate-controlling mechanisms. However, recent work by Langdon and Dorn (33) has shown that a pseudo-Peierls mechanism probably is rate controlling in ordered Cu₃Au at temperatures <100°K, and in disordered Cu₃Au at temperatures <120°K. Previous to this work, the Peierls-Nabarro mechanism was taken to be predominant only in the more open body-centered cubic structures, where it has been demonstrated that the strain rate and temperature dependence of the flow stress can in fact be attributed to the Peierls-Nabarro stress (6).

At low temperatures in face-centered cubic materials, intersection is generally the primary thermal obstacle. By intersection is meant the cutting of "forest" dislocations, which are threading the glide plane, by glissile dislocations moving in the glide plane. In the work of Langdon and Dorn, the intersection process was observed to commence between 220° and 340°K.

In the intermediate temperature range between about 0.25Tₘ and 0.50Tₘ, thermally activated cross-slip can operate. This is certainly true in aluminum, for instance, where the stacking fault energy is quite high. The probability of cross-slip being important in nickel and the nickel-copper system is less because the stacking fault energy is only
moderately high, and decreases rapidly as copper is added (11).

The interaction of dislocations with interstitial atoms is known to be a common mechanism in body-centered cubic metals, although it has not been regarded as important in most face-centered cubic structures. However, it has been demonstrated in the case of thorium (14), a face-centered cubic transition element, that the observed values of activation volume and activation energy, as well as the critical temperature where \( \tau^* \) approaches zero, can all be satisfactorily explained by Friedel's random solute barrier model (34). The Friedel model assumes the interstitial or impurity atoms to represent an array of randomly dispersed rigid obstacles to dislocation glide in the lattice. It predicts the stress temperature relationship to have the following forms;

\[
\tau - \tau_\mu = \tau^* = (\tau_0 - \tau_\mu)(1-T/T_a)^n \quad \text{for } T < T_a \tag{13}
\]

and,

\[
\tau - \tau_\mu = \tau^* = 0 \quad \text{for } T > T_a . \tag{14}
\]

\( T_a \) is the critical temperature where the temperature dependent portion of the flow stress extrapolates to the extended athermal component. The quantity \( \tau_0 \) is simply the flow stress at 0\(^\circ\)K. The exponent \( n \) depends upon the
atomic concentration of solute $c$ where,

$$n = 1, \ c > 10^{-4}$$

and,

$$n = \frac{3}{2}, \ c < 10^{-4}.$$ 

The effective flow stress at absolute zero depends upon $c$ according to the following relationships

$$\tau_0^* = \frac{\mu c}{10}, \ c > 10^{-4} \quad (15)$$

and,

$$\tau_0^* = \frac{\mu c^2}{30}, \ c < 10^{-4}.$$ 

Friedel's model also predicts certain forms of the activation volume. In the case where solute concentration is low, $c < 10^{-4}$,

$$\frac{v}{b^3} = 2\left[\left(1-T/T_a\right)c\right]^{-\frac{1}{2}}, \ T<<T_a \quad (17)$$

and

$$\frac{v}{b^3} = 2\left[\frac{(\tau_0^*-\tau_\mu)/(\tau_0^*-\tau_\mu)}{c}\right]^{\frac{1}{3}} - \frac{1}{3} - \frac{1}{2}, \ T<<T_a \quad (18)$$

Where $c > 10^{-4}$,

$$\frac{v}{b^3} = \frac{a}{2c}, \ T<T_a, \ \frac{1}{3} \leq a \leq \frac{1}{2}.$$ 

Finally, the activation energies are

$$\Delta G = 15kT_a, \ c < 10^{-4} \quad (20)$$
and,
\[ \Delta G \approx 25kT \exp(-c) \quad c > 10^{-4}. \] 

(21)

In Friedel's model, there is no distinction made between substitutional or interstitial solutes. Further, although much of his discussion relates to body-centered cubic structures, the model does not exclude closest-packed structures. The important restrictions are that the impurity or solute atoms be randomly distributed and rigid in the lattice. Accordingly, it is implicit that the formation of Cottrell atmospheres (35) on dislocations, or clustering of the solute atoms, should cause the Friedel mechanism to break down.

Friedel notes that the random solutions required for the model to apply can in principle be obtained by rapid quenching or by pre-strain. Thus, the fact that the solution may not be in thermodynamic equilibrium is not considered.

C. Strain Rate Sensitivity

A useful parameter in mechanical property studies is the strain rate sensitivity, which is frequently given as (36)

\[ m = \frac{\Delta \ln \sigma}{\Delta \ln \dot{\varepsilon}} = \frac{\ln \sigma_2/\sigma_1}{\ln \dot{\varepsilon}_2/\dot{\varepsilon}_1}. \] 

(22)

It is apparent that this quantity is determined from
instantaneous strain rate change tests. The parameter m is of further interest because it is inversely proportional to the Gibbs free energy of activation for a dislocation mechanism, Equation (9).

Another strain rate parameter which is useful in evaluating deformation characteristics is \( \frac{\Delta \sigma}{\Delta \ln \dot{\varepsilon}} \), which is inversely proportional to the activation volume \( v \). It has been noted that this quantity for most face-centered cubic metals is not large and is almost constant (9) with temperature. A notable exception is thorium (14) which at low temperatures has a small value, increases to a maximum at about 250\(^\circ\)K, and then decreases. This behavior is more like the body-centered cubic metals and in the case of thorium, is exaggerated by increasing carbon content (15). The behavior of \( \frac{\Delta \sigma}{\Delta \ln \dot{\varepsilon}} \) is summarized in Figure 5 for several metals.

Another aspect of the strain rate sensitivity of face-centered cubic metals is the behavior of \( \Delta \sigma \) vs. \( \sigma \) plots at constant temperature derived from instantaneous strain rate change tests. It is frequently observed that such plots are straight lines which pass near or through the origin. Cottrell and Stokes (37) were the first to observe this behavior in their experiments on aluminum single crystals, hence it is called Cottrell-Stokes behavior. It should be noted that Cottrell and Stokes performed temperature change tests at constant strain rate and strain, and found a
Figure 5. Variation of $\Delta \sigma/\Delta \ln \varepsilon$ with temperature. Data for iron, copper, aluminum, and thorium are shown (14).
constancy of the ratio $\sigma_{T_2}/\sigma_{T_1}$ beyond about 10% elongation. However, the linear $\Delta\sigma$ vs. $\sigma$ plots noted above, or constant values of $\sigma_{\dot{\varepsilon}}/\sigma_{\dot{\varepsilon}}$ at constant temperature and strain are also taken as valid indicators of Cottrell-Stokes behavior.

When true Cottrell-Stokes behavior is observed, a $\Delta\sigma$ vs. $\sigma$ plot will be of the form

$$\Delta\sigma = k_1\sigma$$

(23)

or

$$k_1\sigma_{\dot{\varepsilon}}_1 = \sigma_{\dot{\varepsilon}}_2 - \sigma_{\dot{\varepsilon}}_1.$$

Upon rearrangement we have

$$\frac{\sigma_{\dot{\varepsilon}}_2}{\sigma_{\dot{\varepsilon}}_1} = (k_1+1) = k_2.$$ 

(24)

Sometimes, although a linearity of $\Delta\sigma$ vs. $\sigma$ is observed, the line does not pass through the origin. This has been observed, for instance, in Cu-2 w/o Co (38). In such cases, Equation (23) would become

$$\Delta\sigma = k_3 + k_1\sigma$$

(25)

or,

$$\sigma_{\dot{\varepsilon}}_2 - \sigma_{\dot{\varepsilon}}_1 = k_3 + k_1\sigma_{\dot{\varepsilon}}_1.$$
It is well established that Cottrell-Stokes behavior is followed in nickel (7) and copper (39). There are no data regarding the nickel-copper system however. In thorium, the "Cottrell-Stokes law" is not followed, even though thorium is face-centered cubic (14). Further, the behavior is not observed in body-centered cubic materials.

D. Interstitials in Face-Centered Cubic Structures

Interstitial atoms in face-centered cubic structures preferably occupy the octahedral sites. Equivalent sites are the cube center and cube edges. Thus an interstitial atom is surrounded symmetrically by 6 nearest neighbor atoms of the host lattice. Such an arrangement causes a spherical distortion when an interstitial is introduced into an octahedral site. In principle, therefore, only edge dislocations should interact with the interstitial in the case of isotropic elastic dislocation theory. However, this view is probably oversimplified, and mechanisms have been proposed whereby tetragonal distortions can be produced in face-centered cubic lattices (40, 41). In particular, Diamond and Wert (22) have proposed and experimentally justified in nickel-carbon an interstitial pair configuration to explain the predominant contribution to an internal friction peak they observed. The simplest pair would consist of two atoms occupying nearest neighbor octahedral sites, such as \( \frac{1}{2} \langle 001 \rangle \) and
This configuration is called a <110> pair and would produce a tetragonal distortion, and so could cause interactions with screw as well as edge dislocations. Fleischer (42) has pointed out that the interaction energy between an interstitial atom and glissile dislocations is proportional to the tetragonality of the strain field produced by the interstitial. This condition applies, irrespective of structure. The addition of carbon to nickel contributes significantly to strengthening (8, 18) especially at low temperatures and higher strains, suggesting a rather strong interaction between the carbon atoms and glide dislocations, as discussed earlier.

E. Electronic Structure and Mechanical Properties

Nickel is a transition element with an electron-deficient 3d shell. Its outer shell configuration is $3d^84s^2$. It is well established that additions of copper, whose shell configuration is $(3d^{10})4s^1$, tend to fill the 3d shell of nickel (13). However, as pointed out by Harris et al. (11), the nature of this filling is not as simple as previously thought and is not completely understood. In fact, their data suggest that empty d-states persist in the system even at high copper concentrations.

The effect of electronic structure on the mechanical properties of metals has not been considered very extensively.
In the work of Harris et al., it was shown in the nickel-copper alloys that d-band filling mainly tended to lower the stacking fault energy of the system. This is shown in Figure 6. Beyond about 50 atomic percent further additions of copper caused a slight rise in the stacking fault energy, then another rather gradual decline toward the value for pure copper. The point is, however, that the width of stacking faults, which is inversely proportional to the stacking fault energy, affects the ability of a system to cross-slip during the deformation process, and so in this way the electronic structure could influence mechanical properties.

Nicholson (43) found that the solubility of carbon in the nickel-copper system decreased as the copper level was increased. Actually, the solubility was nearly constant out to about 30 a/o copper, then decreased rapidly. At 60 a/o copper the solubility decreased slowly to its minimum value at pure copper. Nicholson's work is summarized in Figure 7. Nicholson attributed this behavior to changes in the structure of the 3d level of the system. However, since the solubility behavior did not parallel saturation magnetization behavior, which is a function of the holes in the 3d level, Nicholson concluded that solubility was probably more dependent on the density of states at the Fermi surface. Low temperature specific heat data (44, 45) tended to support his conclusion.
Figure 6. The variation of stacking fault energy with composition in the nickel-copper system (11)
Figure 7. The solubility of carbon in the nickel-copper system as a function of composition at 1000°C (43)
Since electronic structure can influence solubility, it probably influences the interaction of the carbon atom with the host matrix. If this is so, the effect of carbon on the mechanical properties of the nickel-copper system would in turn be affected. Since thorium is also a transition element, the large influence of carbon on the strength of thorium could be related to the establishment of strong bonds between the carbon atoms and the surrounding thorium atoms, and the perturbation of local electronic states in the vicinity of a dislocation.

Zackay et al. (46) considered the influence of d-level electrons on the plastic properties of nickel-iron and nickel-cobalt alloys. They found that additions of cobalt had little influence on stress-strain curves and lattice parameters. On the other hand, additions of iron had a large influence on both of these features. The change in unpaired 3d orbit electrons, $\Delta \mu_B$, in going from cobalt to nickel is 1.10, and from iron to nickel is 1.61. Since significant property changes were noted when adding iron to nickel and not cobalt to nickel, Zackay et al. concluded that the structure of the 3d level was not an important consideration. They noted, however, that the 4s level was altered considerably by adding iron to nickel, and since marked property changes were observed, then 4s level bonding in that particular system was probably more important than the structure of the
3d level. Further, only a small discontinuity in the flow stress was observed at the Curie temperature, further strengthening their argument. In the same category, Diamond and Wert (22) found that magnetic spin ordering, i.e., passing through the Curie temperature, had very little influence on the diffusion of carbon-carbon pairs in nickel.

F. Suzuki Hardening

In a substitutional system such as nickel-copper, the possibility of a Suzuki (47) type of strengthening exists, which might be manifested by an increasing yield drop upon successive aging treatments. Blakemore (5) briefly considered the existence of such a mechanism in nickel-copper, but rejected the possibility due to the relatively high stacking fault energies involved, on the order of 150 ergs/cm² (11), and which increase as the temperature is raised (48).

Hirth and Lothe (49) have pointed out that Suzuki segregation depends upon at least short range diffusion. This, of course, introduces the possibility of a drag-type of behavior where the solute diffuses along with glissile dislocations. This kind of effect would be difficult to separate from Cottrell atmosphere behavior.
III. EXPERIMENTAL PROCEDURE

A. Alloy and Specimen Preparation

The nickel-copper alloys were prepared from \( \frac{1}{2} \) inch diameter 99.985 nickel "270" rod in the hot finished and tempered condition obtained from the Huntington Alloys Division of International Nickel, and 99.999 copper obtained from Cominco Products Inc. The analysis of the as-received nickel rod is given below.

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>99.985</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.0005</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.0010</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.0010</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.0010</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.0007</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.0080</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>0.0024</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.0002</td>
<td></td>
</tr>
</tbody>
</table>

Carbon additions were made from spectroscopically pure Union Carbide graphite electrodes.

The nickel and copper were weighed out on a triple beam balance, and the carbon on an analytical balance. The alloys were weighed in batches of 200 grams.

Melting was accomplished in a tungsten arc furnace under a static atmosphere of argon. A zirconium button was placed in the system as an oxygen getter. During the melting operation, the alloy was turned 8 or 9 times to insure
uniformity of composition. The resultant "ingot" in all cases was an alloy finger roughly 7 inches long and 1/2 inch in diameter.

After melting, each alloy finger was cold swaged down to 0.375 inches in diameter. When swaging was completed, the alloy rods were bright-dipped in a solution of 21% H₂O, 32% H₂SO₄, and 47% HNO₃. Next they were thoroughly rinsed in distilled water and dried in alcohol.

All the alloys were then sealed off in quartz tubes under a vacuum of 10⁻⁶ Torr. Several tantalum strips were placed in each tube with the alloy rod to act as an oxygen getter. Each alloy was next homogenized for 10 days at 1050°C in a muffel furnace. When the homogenization treatment was done, every alloy rod was given a skinning cut on a lathe of about .005 inches to remove any contamination and tantalum which may have adhered to the surface. Small pieces were cut from random alloy rods and metallographically prepared to check the microstructures for segregation. No segregation was detected, thus confirming that the alloys were in fact homogeneous. The resulting alloy compositions and their coded designations are given in Tables 2 and 3. The values for copper and carbon in Table 1 are in atomic percent. Those for oxygen, nitrogen, and hydrogen are in parts per million by weight, and were determined by vacuum fusion. Carbon was determined by a combustion method, and copper
Table 2. Quantitative analyses of alloys used in testing program

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-A</td>
<td>0.00</td>
<td>0.04</td>
<td>8</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>I-B</td>
<td>14.99</td>
<td>0.01</td>
<td>5</td>
<td>ND</td>
<td>&lt;1</td>
</tr>
<tr>
<td>I-C</td>
<td>29.72</td>
<td>0.02</td>
<td>7</td>
<td>ND</td>
<td>&lt;1</td>
</tr>
<tr>
<td>I-D</td>
<td>44.88</td>
<td>0.00</td>
<td>8</td>
<td>ND</td>
<td>1</td>
</tr>
<tr>
<td>I-E</td>
<td>59.62</td>
<td>0.01</td>
<td>4</td>
<td>ND</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-A</td>
<td>0.00</td>
<td>0.18</td>
<td>5</td>
<td>ND</td>
<td>&lt;1</td>
</tr>
<tr>
<td>II-B</td>
<td>14.86</td>
<td>0.18</td>
<td>10</td>
<td>ND</td>
<td>&lt;1</td>
</tr>
<tr>
<td>II-C</td>
<td>29.44</td>
<td>0.16</td>
<td>6</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>II-D</td>
<td>44.88</td>
<td>0.19</td>
<td>4</td>
<td>ND</td>
<td>&lt;1</td>
</tr>
<tr>
<td>II-E</td>
<td>59.70</td>
<td>0.18</td>
<td>4</td>
<td>ND</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

\(^{a}\)It should be noted that the actual chemical analyses were done on tensile specimens. Three specimens of each alloy were randomly selected for the quantitative copper and carbon analyses, and the average of these three is reported in Table 2.

gravimetrically. No compositions above 60 a/o Cu were made up because beyond that composition the solubility of carbon drops to nearly zero at room temperature and 500 ppm by weight at 1000°C (43). An important consideration in these experiments was that all the carbon be in solution.

Table 3 is a qualitative analysis for various elements
Table 3. Qualitative analyses for trace elements in the alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>P</th>
<th>Si</th>
<th>Ta</th>
<th>W</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-A</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>I-B</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>I-C</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>I-D</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>I-E</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>P</th>
<th>Si</th>
<th>Ta</th>
<th>W</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-A</td>
<td>ND</td>
<td>ND</td>
<td>T</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>II-B</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>FT</td>
<td>T</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>II-C</td>
<td>ND</td>
<td>ND</td>
<td>T</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>T</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>II-D</td>
<td>ND</td>
<td>ND</td>
<td>T</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>II-E</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

of interest. The values were obtained by emission spectroscopy. The letters stand for the following: T=trace; FT=faint trace; ND=not detected.

The rods were then cold swaged in several steps down a diameter of 0.096 inches. These alloy wires were next cut to lengths of 2 inches, the final length of the tensile specimens. The cold swaging operation from 0.375 to 0.096 inches was accomplished with little difficulty.

Heat treatment of the cold worked specimens had to be done so that the following conditions were met; 1) the grain
size over the entire composition range from pure nickel to Ni-60 a/o Cu had to be reasonably constant, 2) the grain size had to be small enough so that deformation would be uniform, 3) the heat treating temperature had to be high enough in each alloy so that all the carbon would be in solution, and 4) quenching had to be sufficiently rapid to retain carbon in solution. Accordingly, a heat treating study was carried out. The times and temperatures for each alloy are given in Table 4. The final grain diameter was about .08 mm, as determined by

Table 4. Final heat treatments of the alloys (Series I and II)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature, °C</th>
<th>Time, Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>820</td>
<td>15</td>
</tr>
<tr>
<td>B</td>
<td>1050</td>
<td>15</td>
</tr>
<tr>
<td>C</td>
<td>1050</td>
<td>22.5</td>
</tr>
<tr>
<td>D</td>
<td>1050</td>
<td>15</td>
</tr>
<tr>
<td>E</td>
<td>1000</td>
<td>15</td>
</tr>
</tbody>
</table>

the method of linear intercepts.

Rapid quenching was a necessity principally to suppress graphitization in the Series II (high carbon) alloys. This, then, provided as nearly as possible a random distribution of interstitial solutes. However, so that all the specimens would have experienced approximately the same
treatment, the Series I alloys were also rapidly quenched.

The standard technique of fracturing quartz specimen tubes under some quenching medium (usually brine) proved not to be very satisfactory as a reliable quenching method. This is because it was too slow, taking a few seconds to transfer a tube from the furnace, get it immersed and then fractured. Secondly, this method damaged many specimens and so rendered them useless. As a result, another quenching arrangement was worked out. This consisted of a small kanthal-would tube furnace with a 6 mm ID quartz tube inserted down the axis. The overall length of the furnace was 14-1/2 inches. The hot zone was uniform over about 3 inches. The quartz tube was centered with plugs of firebrick at each end of the furnace. For a quenching run, tantalum strips were placed in the tube to scavenge oxygen, helium purging was started, and the furnace brought to temperature. The helium was grade A and went through a Drierite-Ascarite drying train prior to entering the quartz tube. The exit side was sent through a bubbler to assure positive helium pressure. When temperature was attained, the hose on the exit side was disconnected, two specimens quickly inserted into the hot zone, and the hose then reconnected. The furnace was tilted slightly with the exit end down, so that no outside atmosphere could displace the lighter helium in the system. After the specimens were at temperature for the required length of time,
the exit hose was again disconnected and the furnace quickly up-ended over a container of brine. The specimens slid out of the hot zone and were quenched in a fraction of a second. The bottom of the brine container was padded with cotton so that no hard surfaces were struck.

The specimens acquired a light tarnish from this operation, which easily electropolished off.

After the solution treatment, the specimens were cleaned and then masked at each end for 1/2 inch with stop-off lacquer. The exposed 1 inch of gauge length in the center was then electropolished. The polishing solution was 64% H₃PO₄, 9% H₂SO₄, and 27% H₂O. A cylindrical stainless steel electrode was used and the power settings were 5 v and 2.5 a. During polishing the specimen was slowly rotated. About .002 to .005 inches were typically polished from the diameters. The samples were polished for 90 seconds and then inverted and polished for another 90 seconds, which caused the diameter to be uniform within ± .001 inches.

For the strain aging studies, some wires of Ni-45 a/o Cu were swaged to .065 inches and cut to 2-inch lengths. These were sealed in quartz tubes at 10⁻⁶ Torr, and heat treated at 700°C for 60 minutes. The sample tubes were then removed from the furnace and air-cooled. Further preparation then proceeded as previously discussed. This heat treatment resulted in a very fine grain size, about 12 microns on the
average. These samples, when tested, showed a yield-drop phenomenon not seen in the large-grained alloys. Accordingly, they were used in aging studies wherein a return of the yield point was sought.

B. Testing Program

1. Constant strain rate tensile tests

Tensile tests were conducted with an Instron Model TTC testing machine at a strain rate of $8.33 \times 10^{-5}$ sec$^{-1}$. The specimens were held in pin vise grips with serrated collets so that slipping was eliminated. Each end of the specimens had a 1/2 inch unpolished portion which served as the gripped region. Since a 1-inch gauge section was used, strain rate was simply determined from cross-head speed. In order that the tests could be carried out at a variety of temperatures, a Polanyi type cage was fastened to the cross-head of the Instron machine. This arrangement made it possible to immerse the specimens in baths of varying temperatures.

Tests were done at 5 different temperatures which are shown below along with the corresponding baths.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>78° K</td>
<td>Liquid nitrogen</td>
</tr>
<tr>
<td>193° K</td>
<td>Dry ice and acetone</td>
</tr>
<tr>
<td>298° K</td>
<td>Air</td>
</tr>
<tr>
<td>403° K</td>
<td>Heated silicone oil</td>
</tr>
<tr>
<td>523° K</td>
<td>Heated silicone oil</td>
</tr>
</tbody>
</table>
The silicone oil was heated with an immersion heater and was constantly stirred to maintain a uniform temperature throughout the bath. A thermocouple was attached to the Polanyi cage a fraction of an inch from the gauge section of the specimen. The temperature was controlled by a Brown Pyr-O-Vane off-on controller. During testing, the temperature was maintained to within $\pm 1^\circ$ K of the set-point.

Typically, a specimen was immersed in a particular bath for about 10 minutes before commencing the test. This allowed the specimen, grips, and cage all to come up to the same temperature and so eliminate temperature variations in the system during testing.

The sensitivity of testing was increased through the use of an expanded scale and stepped zero suppression. This enabled the load-elongation trace to be read with much better precision than would normally be possible. Loads could be read from the chart to the nearest 1/10 pound.

Load-elongation data were translated to the more useful true stress-true strain by a computer program. In addition to a tabulated printout, the computer plotted the data through the use of an incremental plotter. Points were placed to within $\pm .01$ inches of the actual value.

The machine deflection or softness had to be determined at each temperature because specimen elongation was determined by cross-head motion and not an extensometer. This was done
by substituting a heavy rigid member for the specimen and running the machine up to about 500 pounds of load at a strain rate of $8.33 \times 10^{-5}$ sec$^{-1}$. Machine deflection was read from the strip chart. This information was fed into the computer along with the standard load-elongation data with the result that machine deflection was automatically subtracted from apparent specimen elongation to give the actual elongation.

2. **Strain rate change tests**

   Instantaneous strain rate change tests were done on all 10 alloys at each of the 5 temperatures. They were conducted in order to 1) obtain information on the strain rate sensitivity of the flow stress through the quantity

   \[
   \frac{\Delta \sigma}{\Delta \ln \dot{\varepsilon}} = \frac{\Delta \sigma}{\ln (\dot{\varepsilon}_1/\dot{\varepsilon}_2)} ,
   \]

   2) have the quantity $(\Delta \ln \dot{\varepsilon}/\Delta \ln \sigma)$ which is proportional to the activation energy of the rate-controlling dislocation mechanism, 3) have $(\Delta \ln \dot{\varepsilon}/\Delta \sigma)$, a quantity proportional to the activation volume, and 4) obtain the variation of $\sigma_{\dot{\varepsilon}_1}/\sigma_{\dot{\varepsilon}_2}$ with $\dot{\varepsilon}_1$, so that the validity of the Cottrell-Stokes law in the nickel-copper and nickel-copper-carbon systems could be evaluated.

   Tests were conducted on the Instron machine between $\dot{\varepsilon}_1 = 8.33 \times 10^{-5}$ sec$^{-1}$, the base strain rate, and
\[ \dot{\varepsilon}_2 = 8.33 \times 10^{-4} \text{ sec}^{-1}. \] As a result, all strain rate ratios were 10:1. The procedure was to start pulling the specimen at the base strain rate to an elongation of about 2%. This was to insure that deformation was essentially all plastic. At this point the strain rate was changed through a push-button control on the Instron. Thus, the strain rate change could be considered instantaneous. The chart speed was also changed at the same instant so that 1 inch of chart represented 1% elongation at both \( \dot{\varepsilon}_1 \) and \( \dot{\varepsilon}_2 \). Elongation at \( \dot{\varepsilon}_2 \) was allowed to proceed for about 1% and then the strain rate was changed back to \( \dot{\varepsilon}_1 \). This procedure of cycling between \( \dot{\varepsilon}_1 \) and \( \dot{\varepsilon}_2 \) every 1% elongation was followed out to the limit of the test, which was usually 20 or 21% total elongation. As a result, 18 to 20 strain rate changes were accomplished with each specimen. In the analysis of the data, however, only the positive strain rate changes were used, that is from \( \dot{\varepsilon}_1 \) to \( \dot{\varepsilon}_2 \), because it was easier to obtain a more accurate \( \Delta \sigma \) from them.

The strain rate changes gave load changes ranging from about (+) 5 pounds to (-) 1 pound, depending on the temperature, elongation, and particular alloy.

The data from strain rate change tests was also fed into the computer for calculation of the parameters mentioned.
3. Strain aging experiments

These tests were conducted on the very fine grained Ni-45 a/o Cu alloy mentioned earlier. In an attempt to study the effects of aging on the yield point in this particular alloy, a variety of aging times and temperatures were incorporated. These various aging conditions are outlined in Table 5.

Table 5. Aging treatments

<table>
<thead>
<tr>
<th>Run</th>
<th>Test temp. °C</th>
<th>Age temp. °C</th>
<th>Age time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R. T.</td>
<td>R. T.</td>
<td>Varying (aged under load)</td>
</tr>
<tr>
<td>2</td>
<td>R. T.</td>
<td>200°</td>
<td>18 hours</td>
</tr>
<tr>
<td>3</td>
<td>180°</td>
<td>180°</td>
<td>Varying (aged under load)</td>
</tr>
<tr>
<td>4</td>
<td>R. T.</td>
<td>650°</td>
<td>30 min. before test; 1 hour at 650°C</td>
</tr>
<tr>
<td>5</td>
<td>R. T.</td>
<td>750°</td>
<td>1 hour</td>
</tr>
<tr>
<td>6</td>
<td>R. T.</td>
<td>700°</td>
<td>65 hours</td>
</tr>
<tr>
<td>7</td>
<td>R. T.</td>
<td>No age</td>
<td>No age (as swaged)</td>
</tr>
<tr>
<td>8</td>
<td>R. T.</td>
<td>400°</td>
<td>1 hour</td>
</tr>
<tr>
<td>9</td>
<td>R. T.</td>
<td>600°</td>
<td>1 hour</td>
</tr>
<tr>
<td>10</td>
<td>R. T.</td>
<td>800°</td>
<td>1 hour</td>
</tr>
<tr>
<td>11</td>
<td>R. T.</td>
<td>1000°</td>
<td>1 hour</td>
</tr>
<tr>
<td>12</td>
<td>R. T.</td>
<td>1000°</td>
<td>17 hours</td>
</tr>
</tbody>
</table>
Some additional details about each aging run are warranted.

Run 1 involved straining the specimen 2%, unloading to about 30 pounds, aging for 5 minutes and reloading and elongating another 2%. This procedure was repeated until aging times included 10 minutes, 1 hour, 4 hours, and 18 hours. Aging and testing were done at room temperature.

In the next test, Run 2, the specimen was elongated about 2-1/2%, unloaded completely and aged for 18 hours at 200° C under vacuum. It was then placed back in the Instron and reloaded.

Run 3 was procedurally the same as Run 2 except that aging under load was done at 180° C. Aging times were 5 and 10 minutes, and 1 and 30 hours.

In Run 4, the specimen was aged 30 minutes at 650° C prior to testing. It was then elongated 2%, unloaded completely, and aged 1 hour at 650° C.

The specimen in Run 5 was aged at 750° C for 1 hour and tested at room temperature. In Run 6 the specimen was aged at 700° C for 65 hours and tested at room temperature.

In Runs 7 through 12, an attempt was made to bracket the conditions where the large yield point could be seen. Thus the aging treatments are simply anneals of cold-swaged wire. Note that in Run 7, a wire was tested in the cold-swaged condition.
IV. RESULTS

A. Stress-Strain Relations

The curves of true stress vs. true strain are shown in Figures 8 through 12, for all 10 alloys at 78°K. It can be seen in Figure 8 that the addition of carbon to nickel has increased the strength level at less than about 0.10 true strain, but an associated decrease in the rate of work hardening has caused a strength decrease at higher strains. In the other alloy systems, carbon seems to have had little effect on the work hardening rate, but has increased the strength level.

In this study, the relationship of flow stress to temperature at constant strain is of more importance. Such plots are constructed from stress-strain curves at various temperatures. Flow-stress temperature curves at 2% engineering strain for the 10 different alloys are given in Figures 13, 14, and 15. Curves at higher strains are of the same form but with the stress levels displaced upwardly. The striking feature of the flow-stress temperature curves is the relatively strong temperature dependence of the stress below about 200°K. This behavior is typical of body-centered cubic metals, but not face-centered cubic. An exception is thorium.

The flow stress at 2% engineering strain and 78°K is
Figure 8. Stress-strain curves for alloys I-A and II-A at 78°K
Figure 9. Stress-strain curves for alloys I-B and II-B at 78°K
Figure 10. Stress-strain curves for alloys I-C and II-C at 78 °K.
Figure 11. Stress-strain curves for alloys I-D and II-D at 78°K
Figure 12. Stress-strain curves for alloys I-E and II-E at 78°K
Figure 13. Flow stress-temperature curves for alloys I-A, II-A, I-B, and II-B
Figure 14. Flow stress-temperature curves for alloys I-C, II-C, I-D, and II-D
Figure 15. Flow stress-temperature curves for alloys I-E and II-E
shown as a function of copper concentration in Figure 16. It is apparent that the peak strength level occurs between 30 and 45 a/o Cu. This is about the same range where Osswald (3) found the maximum critical resolved shear stress in the Ni-Cu system. Again, the general form of this curve is essentially the same for different strain levels and temperatures, but the magnitudes of the stresses are shifted accordingly. Addition of carbon has simply increased the stress level.

B. Serrated Plastic Flow

The phenomenon of serrated plastic flow, also called the Portevin-Le Chatelier effect, was seen in all the high carbon alloys tested except Ni-60 a/o Cu - .2 a/o C. Further, the effect was noted at 403°K in "pure" nickel (which contained .04 a/o C). The other low carbon alloys did not exhibit serrated flow under the temperature and strain rate conditions of this test program. The serrations in nickel were slight, and covered an approximate strain range from 1/3% to 6%.

In Ni - .2 a/o C, serrations first appeared at 298°K. They were present between 1/2% and 12% strain, and were heaviest between 2% and 6% strain. In this range the maximum observed load drop was about 1 pound. This part of the load-elongation curve is shown in Figure 17(a), along with typical regions from the other alloys which exhibited serrated flow.
Figure 16. Flow stress at 2% engineering strain as a function of composition at 78°K.
Figure 17. The Portevin-Le Chatelier effect in nickel-carbon and nickel-copper-carbon alloys. Each square covers a strain range of 2% and a load range of 20 pounds.
At 403°K, alloy II-A, Ni - 0.2 a/o C, underwent serrated flow over the entire strain range, commencing at about 1/2%. The period of the load drops increased with strain, and showed a remarkable regularity. The maximum load drop was about 6 pounds, and occurred in the range between 5% and 15% strain. Beyond that, the amplitude decreased slightly. No serrated flow was observed in Ni - 0.2 a/o C at 523°K, the highest test temperature used.

In Ni -15 a/o Cu - 0.2 a/o C (alloy II-B) very slight serrations starting at about 3/4% strain were noted at 403°K. The load drops were small, less than a pound, but were regularly spaced. The last of these small load drops occurred at about 8% strain. At 523°K, the serrated flow was very heavy. Regularity was again evident, and both the period and amplitude increased with strain. Discontinuous plastic flow persisted from about 1% strain out to the limits of the test, about 20% strain. The largest load drop was 7 pounds. Serrations were observed in Ni-30 a/o Cu - 0.2 a/o C (alloy II-C) at 523°K only. They commenced at about 3% strain and persisted throughout the test. Again, the amplitude and period tended to increase with strain. The maximum load drop was about 3 pounds. The serrations in II-C were not nearly as exaggerated as those in II-B.

Ni -45 a/o Cu - 0.2 a/o C (alloy II-D) exhibited only very slight serrations, confined mainly to strains between 2-1/2%
and 9%, and at 523°K only. The load drops were no more than about 1/2 pound.

As noted previously, Ni-60 a/o Cu -.2 a/o C showed no serrated flow.

These results show that as copper is added to the system, the temperature where serrated flow is first observed increases. This is in basic agreement with the work of Blakemore (5). It should be noted, however, that since Blakemore used a faster strain rate (1.37 x 10^{-4} sec^{-1}) and lower carbon concentration (≈ .1 a/o C), the temperatures he observed are higher than the ones in this work. Further, he found the serrations to disappear at about 35 a/o Cu, whereas they were still present to a slight degree at 45 a/o Cu in the present experiments.

C. Strain Rate Change Tests

The parameter $\Delta \sigma / \Delta \ln \dot{\varepsilon}$ obtained from instantaneous strain rate change tests is shown plotted as a function of temperature at 2% and 5% elongation for each alloy in Figures 18 through 22. In nickel and Ni -.2 a/o C there is a temperature range where $\Delta \sigma / \Delta \ln \dot{\varepsilon}$ is negative, i.e., a negative strain rate sensitivity (SRS). This condition is not observed in any of the other alloys.

At 2% elongation in all of the alloys the $\Delta \sigma / \Delta \ln \dot{\varepsilon}$ parameter goes through a maximum. In Ni and Ni -.2 a/o C
Figure 18. Variation of $\Delta \sigma / \Delta \ln \varepsilon$ with temperature for alloys I-A and II-A at 2% and 5% engineering strain.
Figure 19. Variation of $\Delta \sigma / \Delta \ln \varepsilon$ with temperature for alloys I-B and II-B at 2% and 5% engineering strain.
Figure 20. Variation of $\Delta \sigma / \Delta \ln \varepsilon$ with temperature for alloys I-C and II-C at 2% and 5% engineering strain.
Figure 21. Variation of $\Delta \sigma / \Delta \ln \varepsilon$ with temperature for alloys I-D and II-D at 2% and 5% engineering strain.
Figure 22. Variation of $\Delta \sigma / \Delta \ln \varepsilon$ with temperature for alloys I-E and II-E at 2% and 5% engineering strain.
the maximum, which is very flat, occurs between 100° and 200°K. The same temperature range applies to Ni - 15 a/o Cu and Ni - 15 a/o Cu - .2 a/o C. The range is shifted to between 200°K and 300°K in Ni - 30 a/o Cu, Ni - 45 a/o Cu and their high-carbon counterparts. For Ni - 60 a/o Cu and Ni - 60 a/o Cu - .2 a/o the peak Δσ/Δlnε is a little higher still, possibly above 300°K. The important consideration, however, is that the temperature range of maximum SRS increases as copper is added. Carbon appears not to affect this range, but changes the magnitude of Δσ/Δlnε. Further, it is noted that carbon contributes to the SRS over the lower portion of the temperature range, and detracts from it at higher temperatures. The "crossover" point, where Δσ/Δlnε is the same for the low and high carbon alloys at 2% strain moves to higher temperatures as Cu is added.

The fact that Δσ/Δlnε vs. temperature goes through a maximum is a phenomenon generally confined to body-centered cubic metals. Such a maximum has, however, been observed in thorium, a face-centered cubic metal (refer to Figure 5). It is seen in the present work that this behavior is mostly eliminated in the high carbon alloys at higher strains, as little as 5%. This is simply an effect of work hardening.

Another way to look at SRS is the ratio $\sigma_1(\dot{\varepsilon} = .005)/\sigma_2(\dot{\varepsilon} = .05)$, which indicates the fractional increase in flow stress due to a given increase in strain
rate. This ratio is plotted for each alloy as a function of temperature at 2% strain in Figures 23 through 25. Lower values of the ratio indicate a higher SRS. Where $\sigma_1/\sigma_2$ is unity, the SRS is zero, and where $\sigma_1/\sigma_2$ is greater than unity, the SRS is negative. As before, it is seen that carbon contributes to the SRS at lower temperatures, and detracts from it at higher temperatures. The crossover point moves upward in temperature as the copper level is increased. This temperature is plotted as a function of copper concentration in Figure 26(a). Note that two distinct linear portions exist, with the break being at about 30 a/o Cu.

At higher strain levels, greater than about 10%, $\sigma_1/\sigma_2$ approached a constant value, whether or not the Cottrell-Stokes law rigidly applied. In order to determine the effects of work hardening on the crossover temperature, the $\sigma_1/\sigma_2$ ratios for the last three strain rate changes were averaged. This average ratio for each alloy and test temperature was plotted in the same way as those at 2% strain. The results were essentially the same, with rather minor alterations in the temperature of crossover occurring. For comparison, the crossover temperature for each copper level, for low and high strains, is given in Table 6. A plot of the high-strain crossover temperature vs. copper level is given in Figure 26(b). It is essentially linear, the two distinct slopes previously observed presumably being eliminated by the effects of work hardening.
Figure 23. Flow stress ratio as a function of temperature for alloys I-A, II-A, I-B, and II-B
Figure 24. Flow stress ratio as a function of temperature for alloys I-C, II-C, I-D, and II-D
Figure 25. Flow stress ratio as a function of temperature for alloys I-E and II-E.
Figure 26. Composition dependence of the temperature where Series I and Series II have equal flow stress ratios, $\sigma_1/\sigma_2$. 

(a) 2% ENG. STRAIN

(b) >10% ENG. STRAIN
Table 6. Crossover temperature for low and high strains as a function of composition

<table>
<thead>
<tr>
<th>Cu, a/o</th>
<th>$T(2% \varepsilon), ^\circ K$</th>
<th>$T(&gt;10% \varepsilon), ^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>237</td>
<td>200</td>
</tr>
<tr>
<td>15</td>
<td>312</td>
<td>270</td>
</tr>
<tr>
<td>30</td>
<td>403</td>
<td>375</td>
</tr>
<tr>
<td>45</td>
<td>435</td>
<td>460</td>
</tr>
<tr>
<td>60</td>
<td>498</td>
<td>550</td>
</tr>
</tbody>
</table>

Figure 27 shows a $\sigma_1/\sigma_2$ difference "surface". It represents the difference in the flow stress ratio between Series I and Series II alloys as a function of temperature and composition. Where the surface is negative, the SRS was increased by adding carbon. Where it is positive, the SRS was decreased. The surface was constructed from flow stress ratios at strains greater than 10%.

In order to check the applicability of the Cottrell-Stokes "law", $\Delta \sigma$ vs. $\sigma$ plots were constructed. In cases where heavy serrated flow took place, no strain rate sensitivity as such could be defined, although it was probably negative, so $\Delta \sigma$ vs. $\sigma$ plots were not possible. In many cases where linear plots could be made, the intercept at $\sigma=0$ was not zero. That is, $\Delta \sigma$ was of the form expressed by Equation (25). These are summarized in Figures 28, 29 and 30. For nickel, the only
Figure 27. Difference in strain rate ratio between Series I and Series II alloys as function of copper concentration and temperature
Figure 28. The influence of temperature on $\Delta \sigma$ at zero stress in alloys I-A, II-A, I-B, and II-B.
Figure 29. The influence of temperature on $\Delta \sigma$ at zero stress in alloys I-C, II-C, I-D, and II-D.
Figure 30. The influence of temperature on $\Delta\sigma$ at zero stress in alloys I-E and II-E
deviations from C-S behavior were negative. Where there were heavy serrations or negative SRS, the situation was undefined, as noted on the figures. It was observed that C-S behavior persisted up to 193°K for high and low carbon levels. Deviations occurred at 298°K, where nickel had a negative intercept. At the higher carbon level, the SRS was negative.

In Ni-15 a/o Cu, a negative intercept occurred at 523°K. At all other temperatures, the intercept was zero. For Ni-15 a/o Cu -.2 a/o C, heavy serrations were present at 403°K and 523°K making Δσ vs. σ plots impossible. At lower temperatures, C-S behavior was present.

The behavior of Ni-30 a/o Cu was very similar to that of Ni-15 a/o Cu. There was a negative deviation at 523°K. However, in Ni-30 a/o Cu -.2 a/o C there were strong positive deviations at 193°K and 298°K. At 403°K the deviations mostly disappeared, and at 523°K it was undefined due to serrated flow.

In Ni-45 a/o Cu positive deviations from C-S behavior appeared at 78°, 193°, 298°, and 403°K. At 523°K the deviation was negative. The higher carbon alloy paralleled this behavior but the magnitudes of the positive intercepts were greater. The negative one at 523°K was about the same as that for the low carbon alloy. Ni-60 a/o Cu exhibited C-S behavior at all temperatures except 298°K, where a positive deviation was noted. The Δσ for Ni -60 a/o Cu -.2 a/o C was zero at
523°K, and positive at the four lower temperatures.

It should be noted that plots of $\Delta \sigma$ vs. $\sigma$ extrapolated back to zero stress are subject to inaccuracies. This is because in many cases only the last three or four points were used for the extrapolation. Accordingly, only relative trends can be discussed with confidence, and not precise values of the intercepts at $\sigma = 0$.

D. Activation Analysis

The critical temperature, $T_a$, where the temperature dependent portion of the flow stress extrapolates to the extended athermal flow stress was determined from the flow stress-temperature curves shown in Figures 11 through 13. In addition, $T_a$ was calculated from Equation (13), using $T = 78°K$ and $n = 1$ in all cases. The use of $n = 1$ is permissible in the low carbon alloys because the atomic concentration of interstitial impurities was calculated to be about $10^{-4}$ or slightly higher for every alloy of that series. These alloys are then more or less borderline insofar as impurity level is concerned, but the best agreement with experimental values of $T_a$ was obtained by using $n = 1$. Comparison of the experimental and calculated values are given in Table 7. The agreement between these values is very good.

The activation volume was determined experimentally at 78°K and 2% elongation through Equation (5) for each alloy.
### Table 7. Experimental and calculated critical temperatures

<table>
<thead>
<tr>
<th>Cu, a/o</th>
<th>$T_a$, Series I</th>
<th></th>
<th>$T_a$, Series II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
<td>Experimental</td>
<td>Calculated</td>
</tr>
<tr>
<td>0</td>
<td>243°K</td>
<td>239°K</td>
<td>194°K</td>
<td>193°K</td>
</tr>
<tr>
<td>15</td>
<td>245°</td>
<td>245°</td>
<td>242°</td>
<td>250°</td>
</tr>
<tr>
<td>30</td>
<td>312°</td>
<td>312°</td>
<td>247°</td>
<td>248°</td>
</tr>
<tr>
<td>45</td>
<td>335°</td>
<td>343°</td>
<td>220°</td>
<td>224°</td>
</tr>
<tr>
<td>60</td>
<td>265°</td>
<td>240°</td>
<td>227°</td>
<td>216°</td>
</tr>
</tbody>
</table>

For the Series I (low carbon) alloys, the activation volume was calculated with Equations (17) and (18). These equations gave the best agreement with the experimental values. The borderline nature of these alloys is reflected in the fact that Equations (17) and (18) apply when the atomic concentration is less than $10^{-4}$. For the Series II (high carbon) alloys, Equation (19) gave the best agreement with experiment, as expected. The experimental and calculated activation volumes are shown in Table 8.

### Table 8. Experimental and calculated activation volumes

<table>
<thead>
<tr>
<th>Cu, a/o</th>
<th>$v/b^3$, Series I</th>
<th></th>
<th>$v/b^3$, Series II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
<td>Experimental</td>
<td>Calculated</td>
</tr>
<tr>
<td>0</td>
<td>334</td>
<td>370</td>
<td>252</td>
<td>139</td>
</tr>
<tr>
<td>15</td>
<td>311</td>
<td>260</td>
<td>171</td>
<td>132</td>
</tr>
<tr>
<td>30</td>
<td>258</td>
<td>226</td>
<td>108</td>
<td>111</td>
</tr>
<tr>
<td>45</td>
<td>227</td>
<td>239</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>60</td>
<td>191</td>
<td>206</td>
<td>141</td>
<td>132</td>
</tr>
</tbody>
</table>
The experimental activation volumes as a function of copper level are plotted in Figure 31. Experimental activation volumes as a function of the effective stress $\tau^*$ are shown in Figures 32 and 33. Plots for nickel and Ni - .2 a/o C were not made because only two points per alloy were available. The best agreement between the experimental and calculated values occurs at 30, 45 and 60 a/o Cu and in the high carbon Series II alloys.

By use of Equation (9), experimental activation energies, $\Delta G$, were calculated at 2% strain and several temperatures. These values for each alloy, given in Table 9, were determined at 78° and 193°K.

Table 9. Experimental activation energies

<table>
<thead>
<tr>
<th>Cu, a/o</th>
<th>$\Delta G$, Series I</th>
<th>$\Delta G$, Series II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>78°K</td>
<td>193°K</td>
</tr>
<tr>
<td>0</td>
<td>.06 eV</td>
<td>.24 eV</td>
</tr>
<tr>
<td>15</td>
<td>.12</td>
<td>.37</td>
</tr>
<tr>
<td>30</td>
<td>.16</td>
<td>.41</td>
</tr>
<tr>
<td>45</td>
<td>.13</td>
<td>.34</td>
</tr>
<tr>
<td>60</td>
<td>.15</td>
<td>.52</td>
</tr>
</tbody>
</table>

Note that the concentration dependence of $\Delta G$ with respect to interstitials is not significant at copper levels of 30, 45, and 60 a/o.

A determination of the slope of the $\Delta G$ vs. temperature
Figure 31. Activation volume as a function of copper concentration at 2% engineering strain and 78°K in Series I and Series II alloys.
Figure 32. Variation of activation volume with effective shear stress in alloys I-B, II-B, I-C, and II-C
Figure 33. Variation of activation volume with effective shear stress in alloys I-D, II-D, I-E, and II-E
relationship was done in order to make comparisons with Equations (20) and (21). At 0°K AG must go to zero, so the best straight line fit was found for AG between 0°K and 193°K. Beyond 193°K, the critical temperature was approached, and deviations from linearity occurred. The experimental activation energies are plotted against temperature in Figures 34, 35 and 36. The slopes of the linear portions of these plots are summarized in Table 10.

Table 10. Slopes of experimental activation energies vs. temperature

<table>
<thead>
<tr>
<th>Cu, a/o</th>
<th>Slope, AG vs. T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series I</td>
</tr>
<tr>
<td>0</td>
<td>13.4 k</td>
</tr>
<tr>
<td>15</td>
<td>19.7</td>
</tr>
<tr>
<td>30</td>
<td>24.6</td>
</tr>
<tr>
<td>45</td>
<td>22.0</td>
</tr>
<tr>
<td>60</td>
<td>28.5</td>
</tr>
</tbody>
</table>

For solute concentrations greater than 10⁻⁴, the Friedel model predicts a slope of about 25 k. Again, the agreement is very good at the higher copper levels, and especially at 30 a/o Cu.

The final parameter considered was the effective shear stress at 0°K, \( \tau^* \). This was determined experimentally by extrapolating the flow stress vs. temperature curves to 0°K. This quantity as a function of composition is shown in
Figure 34. Activation free energy as a function of temperature for alloys I-A, II-A, I-B, and II-B.
Temperature 35. Activation free energy as a function of temperature for alloys I-C, II-C, I-D, and II-D.
Figure 36. Activation free energy as a function of temperature for alloys I-E and II-E
Figure 37. The effective shear stress at 0°C, $\tau^*$, as a function of composition.
Figure 37. The calculated values were determined from Equations (15) and (16). Table 11 compares the experimental and calculated values of $\tau^*$. 

Table 11. Experimental and calculated effective shear stresses at 0°K

<table>
<thead>
<tr>
<th>Cu, a/o</th>
<th>$\tau^*$, Series I</th>
<th>$\tau^*$, Series II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
</tr>
<tr>
<td>0</td>
<td>0.5098 kg/mm²</td>
<td>0.3706 kg/mm²</td>
</tr>
<tr>
<td>15</td>
<td>1.2418</td>
<td>2.5610</td>
</tr>
<tr>
<td>30</td>
<td>2.3954</td>
<td>2.3740</td>
</tr>
<tr>
<td>45</td>
<td>2.6437</td>
<td>2.4972</td>
</tr>
<tr>
<td>60</td>
<td>2.5228</td>
<td>2.0067</td>
</tr>
</tbody>
</table>

The calculated values for Series II were determined from Equation (15) because $C > 10^{-4}$. Note that the agreement is not good except at the zero copper level. At 15 a/o Cu the calculated value is too low by a factor of 2, and the values at 30, 45, and 60 a/o Cu are off by nearly a factor of 4.

In the Series I alloys, Equation (16) was used for the 15 a/o through 60 a/o Cu alloys. Equation (15) had to be used for nickel because $C = 4 \times 10^{-4}$. The agreement is fair for nickel, and reasonably good for the 30, 45, and 60 a/o Cu alloys.
E. Effect of Carbon on the Flow Stress

It was of interest to determine directly the strengthening effect of carbon as a function of copper concentration at a given temperature and strain. This was done at 0°K by extrapolation of the flow stress vs. temperature curves, and at 78°K where data points existed. The rate of strengthening due to carbon, shown in Table 12, is expressed as $\frac{d\tau}{dc}$ in terms of $\mu$, the shear modulus, for each copper level.

Table 12. The rate of strengthening due to carbon

<table>
<thead>
<tr>
<th>Cu, a/o</th>
<th>$d\tau/dc$, 0°K</th>
<th>$d\tau/dc$, 78°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.25$\mu$</td>
<td>0.17$\mu$</td>
</tr>
<tr>
<td>15</td>
<td>0.42</td>
<td>0.31</td>
</tr>
<tr>
<td>30</td>
<td>0.58</td>
<td>0.35</td>
</tr>
<tr>
<td>45</td>
<td>0.55</td>
<td>0.22</td>
</tr>
<tr>
<td>60</td>
<td>0.45</td>
<td>0.28</td>
</tr>
</tbody>
</table>

F. Strain Aging Experiments

The results of this series of experiments were essentially negative in that under no conditions could the yield point be made to reappear to a significant degree. It was found that a cold worked wire annealed at 600°C for 1 hour showed
no yield point. At 700°, 800° and 1000°C for 1 hour the annealed material exhibited a sharp yield drop. When annealed for 17 hours at 1000°C, there was no yield point. Also, when annealed at 1050°C for 15 minutes the yield drop disappeared. These results show that the initial yield drop is apparently a grain size phenomenon. This is further confirmed by an experiment wherein a wire was annealed at 1050°C for 15 minutes and quenched. It was then annealed for 1 hour at 700°C and slow cooled. No yield drop was observed upon testing.

It was noted, however, that the strain range of discontinuous yielding increased linearly with decreasing temperature between 1000°C and 700°C. This is for a constant annealing time of 1 hour. Below 700°C, recrystallization was not complete. At 1000°C, the strain range was about 0.31. At 700°C it was 0.90. The magnitude of the yield drop also increased with decreasing temperature, but apparently in not as regular a fashion. The load decrease at 1000°C was about 1/2 pound, and nearly 3 pounds at 700°C. It should be noted that although discontinuous yielding took place over a range of strain, there was an observable amount of work hardening in that range. Accordingly, it could not be attributed to a Luders mechanism. In fact, no Luders front was detected in any of the tests.
V. DISCUSSION OF RESULTS
A. Interstitial Effects

It is apparent that all of the alloys except nickel and Ni-.2 a/o C have exhibited some mechanical properties that are more typical of body-centered cubic metals than face-centered cubic ones. Moreover, this kind of behavior is enhanced in the high carbon, Series II, alloys. The constant-strain flow stress vs. temperature data, Figures 13, 14, and 15, demonstrate this very well. Alloys containing 30, 45, and 60 a/o Cu show a relatively strong temperature dependence of the constant strain flow stress at temperatures less than about 300°K. The addition of 0.2 a/o C exaggerates the effect. Even at 15 a/o Cu the flow stress is significantly temperature dependent. Such behavior is common in body-centered cubic metals, but rare in other structures. It has been observed in face-centered cubic thorium (14, 15) and disordered Cu₃Au (33). Further, Flinn (18) found a strong dependence in Ni-.5 a/o C and Ni-1.0 a/o C.

In a face-centered cubic metal, the strain rate parameter \( \frac{\Delta \sigma}{\Delta \ln \varepsilon} \) should be relatively insensitive to temperature, as shown in Figure 5. Again, the exception is thorium. A body-centered cubic metal will normally display a maximum value at some fixed temperature. The Series I and II alloys in this study containing 15, 30, 45, and 60 a/o Cu all showed a
definite maximum at strain levels below about 2\%.^1 The

temperature where the maximum occurred was in the range be­
tween 200° and 300°K. The maximum falls in the same tempera­
ture range for thorium, but this is considered to be merely
coincidental. The important point is that in the nickel-
copper and nickel-copper-carbon alloys that were rapidly
quenched from temperatures well above the solubility tempe­

ture for carbon, mechanical property behavior that is usually
expected of body-centered cubic metals was induced.

Most of the remaining portion of this discussion will be
devoted to rationalizing why it is, in fact, possible to
induce body-centered cubic mechanical property behavior in a
series of face-centered cubic alloys. The results will then
be extended to explain similar results that have been obtained
in thorium (14) and thorium-carbon alloys (15).

All of the experiments point directly to the fact that
the observed mechanical property behavior is associated with
interstitial atoms in the material. Consider first the
Portevin-Le Chatelier effect in nickel-copper-carbon alloys.\(^2\)

\(^1\)Various parameters were compared at constant strain rath­
er than constant stress or effective stress because of the ef­
fects of work hardening. For instance, to look at the activa­
tion volume at constant effective stress would involve the ef­
fects of composition and temperature on work hardening. At con­
stant strain, only the effects of composition changes come into
play. Although it is probably more rigorously correct to make
comparisons at constant effective stress, it is doubtful if any
real advantage is gained when comparing several compositions.

\(^2\)Some criticisms of Blakemore's interpretations are given
in Appendix A.
Blakemore's work (5) showed that as copper was added to the system, the temperature where serrated flow was first observed moved upward. Observations of serrated plastic flow in the present experiments confirmed this, differing only in details. This result is an indication that the mobility of carbon is apparently decreased as the copper level is increased. A more fundamental verification of this is the flow stress ratio, $\sigma_1/\sigma_2$, for Series I and Series II alloys. The results are summarized in Figures 23, 24, and 25. There is a unique temperature at each copper level where the addition of carbon neither adds nor detracts from the strain rate sensitivity (SRS). Below this temperature carbon increases the SRS, and above it carbon reduces the SRS. When carbon contributes to the SRS, it acts as an immobile thermal barrier to dislocation motion in the lattice. Carbon detracts from the SRS when it becomes mobile enough to begin interacting and possibly attaching itself to the stress field of a glide dislocation at the lower strain rate of a strain rate change test. In this situation, an increase in the strain rate may actually cause a drop in the flow stress as glide dislocations begin to move faster than the mobile carbon atoms. The observed $\sigma_1/\sigma_2$ crossover point is assumed to be that temperature where the carbon atoms have characteristics of being rigid thermal barriers and, at the same time, mobile obstacles which pace the moving dislocations. The fact that
this temperature moves upward nearly linearly with copper concentration, Figure 26, is another indication that carbon becomes increasingly immobile as copper is added. The $\sigma_1/\sigma_2$ crossover temperature is actually more definitive than trying to pinpoint the exact temperature where visible serrations occur because it is much more precise. It further shows that the carbon atoms become significantly mobile at a much lower temperature than the onset of serrated plastic flow would indicate. It is tempting to attribute the decrease in carbon mobility to a corresponding decrease in stacking fault energy in the system (refer to Figure 6). However, between 15 and 60 a/o Cu, the changes in stacking fault energy are small and probably insignificant, whereas the changes in carbon mobility are large.

Serrated flow and the $\sigma_1/\sigma_2$ data both gave dynamic evidence of the decreasing mobility of carbon as the copper level was increased. More analytical evidence lies in the "activation analysis" carried out on each of the 10 alloys studied. This was done to ascertain the rate controlling barriers to dislocation motion. It was found that the Friedel random solute barrier (RSB) theory correctly predicted the critical temperature, activation volume, and activation energy in Series I and II alloys containing 30, 45, and 60 a/o Cu. Agreement between theory and experiment appears to be the closest in the 30 a/o Cu range. The reason for this will be
brought out later in the discussion. At these 3 higher copper levels there is no dependence of the activation energy on carbon content. This is further proof that the RSB theory is obeyed in these alloys.

The RSB theory almost applies at the 15 a/o Cu level, but the concentration dependence of the activation energy is too large. Accordingly, this alloy appears to be a marginal case. Probably between 15 and 30 a/o Cu the theory begins to work.

The important correlation is that the RSB theory applies at copper levels where, from independent experiments, it is established that the carbon atoms have become increasingly immobile. At the same time, the alloy system is exhibiting body-centered cubic mechanical property behavior with respect to flow stress vs. temperature as well as $\frac{\Delta \sigma}{\Delta \ln \varepsilon}$ vs. temperature. Thus, behavior that is normally attributed to the fact that a lattice is body-centered cubic or face-centered cubic may, in fact, have little to do with the crystal structure per se. The characteristic mechanical properties previously noted are instead due to the interstitial atoms acting as an array of randomly distributed, rigid, thermal barriers to dislocation motion.

Since it appears that carbon does become more immobile in the presence of increasing amounts of copper, it is now appropriate to rationalize why this happens.
In the nickel-copper system, the lattice parameters and stiffness constants change almost linearly as copper is added. The lattice parameters increase and the stiffness constants decrease. Now consider the strain energy associated with inserting a carbon atom in the octahedral hole of nickel. The diameter of the hole is 1.032Å. The effective diameter of the carbon atom in the diamond lattice is 1.541Å. Based on a hard sphere calculation, the unit cell expands about 14% when a carbon atom is placed in the site. Through use of the relation for strain energy (50),

\[ U = \frac{1}{6}(C_{11} + 2C_{12})\delta^2 \] (26)

where,

\[ \delta^2 = (V/V^0 - 1) \equiv \text{volume strain} \] (27)

the strain energy associated with this operation is 1.58 eV per atom of nickel. As copper is added to the system, the strain energy decreases linearly. At Ni-60% Cu, it is only 1.21 eV per atom. This is a decrease of about 24% from the value at pure nickel. The result is that the octahedral site becomes more stable with respect to accommodating an

1Hard sphere calculations were used throughout because there is no data on the variation of lattice parameters in nickel-copper as carbon is added. Information of this kind is available for nickel and thorium, but the need for consistency dictated using the hard sphere model for them also. A comparison between U obtained from lattice parameters and hard sphere calculations is given in Appendix B.
interstitial atom. From strain energy considerations, it becomes progressively easier for the interstitial to remain in its site. Calculations of the binding energy of an interstitial with an edge dislocation using (51),

\[ W = -\frac{1}{2\pi} \frac{1+\nu}{1-\nu} \mu |\Delta v_a| \]  

\[(28)\]

show that \( W = -0.129 \text{ eV} \) for nickel, and \(-0.092 \text{ eV}\) for Ni-60\% Cu. Thus there is a measurable decrease in the dislocation-interstitial atom interaction energy as copper is added, on the order of 29\%.

In Figure 7, taken from the work of Nicholson, it is seen that the solubility of carbon decreases in the nickel-copper system as copper is added. This is due to an electronic effect, most probably according to Nicholson a decrease in the density of states at the Fermi surface. Note however, that the solubility is virtually constant in the composition range between pure nickel and Ni-30 a/o Cu. This means, of course, that electronic effects are not controlling solubility at low copper levels, or are being offset by the decrease in strain energy. Even at 45 a/o Cu, the carbon solubility is comparatively high, although the decrease in the density of states has become apparent. The main point, however, is that at 30 and 45 a/o the best agreement with Friedel's RSB theory is obtained. The combination of an increase in interstitial site stability due to decreased
strain energy, along with high carbon solubility has made the carbon atoms essentially rigid in their lattice positions. When the solubility of carbon is high, some kind of bonding has probably been established between the carbon atoms and the atoms of the host matrix. This may contribute to the stability of the carbon atoms in their sites. Bonding is probably of a resonating nature. The relatively small size of the octahedral hole would cause the bonds to be quite distorted if they were established between the carbon atom and its 6 nearest neighbor lattice atoms. As a result, a proportion of the bonding must be set up with the 8 next nearest neighbors.

Figure 31 shows that the trend in activation volume is downward as copper is added and as carbon is increased. However, at 60 a/o Cu in Series II, the trend begins to reverse itself, i.e., the activation volume shows a slight increase. The RSB theory is still well obeyed in spite of this trend. A simple rationalization can be made on solubility considerations, namely that at this high copper level all the carbon did not go into solution even though the quench was extremely fast. Accordingly, the carbon in solution is something less than 0.2 a/o. However, the carbon that did actually go into solution is very stable in the lattice. This is substantiated by the fact that the RSB theory is still obeyed and that no serrated flow was observed. Here, then,
is indirect proof that while bonding between the carbon solute atoms and those of the host copper-nickel matrix may contribute in some way to carbon atom rigidity in the lattice, the effect certainly is not controlling because no such bonding could exist at very high copper levels.

The results obtained in the system make it possible to explain with certainty similar observations made by Zerwekh and Scott in thorium (14) and Peterson and Skaggs in thorium-carbon alloys (15). It was noted previously that body-centered cubic type mechanical property behavior was seen in thorium and the thorium-carbon system.

Serrated plastic flow has not been seen in thorium, even at high levels of carbon, low strain rates, and high temperatures. This, of course establishes that carbon atom-dislocation interaction is not large in thorium. A calculation similar to the one carried out for nickel-copper gives a value of $W = -0.005 \text{ eV}$, about an order of magnitude less than that for the nickel-copper system. Thus the tendency for a carbon atom to attach itself to a dislocation is not great. This result indicates that carbon in the octahedral site of thorium is very stable. Some further considerations show why. The lattice parameter of thorium is quite large, being $5.0872\text{Å}$, resulting in an octahedral site diameter of $1.4920\text{Å}$. Since the effective diameter of carbon is $1.5410\text{Å}$, there is little lattice accommodation necessary for a carbon atom to fit in.
Based on a hard sphere calculation, the unit cell of thorium is expanded only about 1 percent when a carbon atom is inserted in the octahedral site. The stiffness constants of thorium are low, so that the resultant strain energy is only 0.006 eV per atom of thorium. This is about 260 times less than that in nickel. Similar to nickel and the nickel-copper system, thorium is a transition element. Its outer shell configuration is $6d^27s^2$ which shields an incomplete 5f shell. This makes possible an electronic interaction of the carbon atoms with the thorium matrix, promoting a thorium-carbon bond, as discussed for the case of nickel. Due to the large size of the octahedral hole, the bond lengths can be almost optimum. Finally, the solubility of carbon in thorium is 3500 ppm by weight, at room temperature which is unusually high for a face-centered cubic metal.

The effects of a very large interstitial site and low values of the stiffness constants contribute to making a carbon atom very rigid in the thorium lattice. As a result, body-centered cubic mechanical property behavior is prominent, and the RSB theory fits exactly.

In thorium-carbon alloys, the mechanical properties were directly influenced by the carbon content. At very low carbon levels, 0.08 a/o, the dependence of flow stress on temperature was essentially eliminated, as was the maximum in the strain rate parameter $\frac{\Delta\sigma}{\Delta\ln\dot{\varepsilon}}$. Both of these dependences increased
uniformly as the carbon level was increased. Similar trends have been noted in the nickel-copper-carbon alloys of this study. In the series II alloys (0.2 a/o C) for example, the change in flow stress between 300°K and 0°K was 13, 15, and 13 Kg/mm² for copper levels of 30, 45, and 60 a/o, respectively. In thorium containing 0.216 a/o C, the increase in flow stress over the same temperature range was 14 Kg/mm².

Some comment should be made concerning the possibility of a Pierels-Nabarro (P-N) mechanism being operative in the nickel-copper-carbon system. According to Ono and Sommer (52), when a P-N mechanism is operative, by way of a nucleation limited double kink process, there should be no concentration dependence of the thermal part of the flow stress. An example of this is seen in dilute solutions of nitrogen in iron (53) in the concentration range between 0.001 and 0.14 a/o N. However, the theory predicts that above a certain composition of solute, dispersed random barriers will become so numerous that they will then dominate strengthening. At this point, a composition dependence of the thermal portion of the flow stress sets in. It is clear that in the case of thorium-carbon alloys dispersed barriers are rate controlling at interstitial contents at least as low as 0.08 a/o (15). In nickel-copper-carbon alloys, randomly dispersed barriers are evidently rate controlling down to levels as low as 0.01 a/o. However, it is apparently possible to have a P-N
mechanism become operative in both of these alloy systems if the levels of impurities could be further lowered.

The Cottrell-Stokes "law" does not apply in thorium, although it is considered a characteristic type of behavior in face-centered cubic metals. Figures 28, 29, and 30 are plots of the stress change extrapolated to zero stress as a function of temperature for each of the ten alloys studied. They show that at 0 a/o and 15 a/o Cu the C-S behavior is followed closely except at temperatures where serrated flow begins. It is of interest to note that where serrations occurred in the high carbon alloy, the low carbon one usually exhibited a negative $\Delta \sigma$ at zero stress. This means that at those particular temperatures, the alloys had an inherent negative SRS due to the mobility of the interstitials. The strongest deviations from C-S behavior occurred in the 30, 45, and 60 a/o Cu Series II alloys. All exhibited marked positive deviations over a broad temperature range. These alloys, of course, are the ones in which it was established that the carbon atoms were rigidly bound. Positive deviations represent the fact that the interstitials can be characterized as an array of thermal barriers to dislocation glide. As such, they constitute an "in situ" positive SRS.

Although the C-S data are more or less qualitative in nature, an important trend is apparent. That is, in those alloys where the RSB theory applied and where body-centered
cubic type mechanical behavior was found, the largest positive deviations from C-S behavior occurred.

The accumulated evidence from this work and the earlier studies carried out in thorium and thorium-carbon alloys confirm that mechanical property behavior that had previously been labeled as typical of body-centered cubic metals actually can be associated with the presence of interstitials, and is a function of the relative rigidity of an interstitial atom in its lattice site. In the nickel-copper-carbon system, where the solubility of carbon is virtually zero at room temperature, interstitials had to be introduced by very rapid quenching from high temperatures. Once introduced in significant quantities, however, body-centered cubic behavior was induced. In thorium, where the solubility of carbon is very high, such behavior is seen without the need for quenching.

B. Carbon Mobility

The data have indicated that the mobility of carbon in the nickel-copper lattice decreases in a regular way with increasing copper content. This is apparently a result of a decreasing strain energy density of the lattice in the immediate vicinity of an interstitial and the changing electronic character of the matrix.

The mobility (net drift velocity) of a species of atom can be defined in terms of the diffusivity as (54),
where \( B \) is the mobility, \( D \) is the diffusivity, and \( R \) and \( T \) have their usual meaning. The \( \sigma_1/\sigma_2 \) crossover temperature was defined as that temperature where the carbon atoms were just beginning to pace the moving dislocations. Since dislocation velocity can be expressed,

\[
\bar{v} = \dot{\varepsilon}/\rho b,
\]

it is a reasonable assumption that at a constant strain level, \( \bar{v} \) is about the same across the range of alloy compositions. If this is the case, then the crossover temperatures for the different alloys express the temperature where the mobility of carbon is the same in all of them. Accordingly, it follows that, at 2% strain,

\[
B(\text{Ni, 237}^\circ\text{K}) = B(\text{Ni-15 Cu, 312}^\circ\text{K}) = \cdots = B(\text{Ni-60 Cu, 498}^\circ\text{K}).
\]

From the work of Diamond and Wert (22) the expression for the diffusivity of carbon-carbon pairs is,

\[
D = 0.048 \exp(-34,800/RT).
\]
equating mobilities at the crossover temperatures. When this is done, the following activation energies of 46,650, 59,540, 65,330, and 72,570 calories per mole are obtained for copper levels of 15, 30, 45, and 60 a/o, respectively.

It could be argued that the carbon mobility was influenced by changes in the pre-exponential term rather than the activation energy. The pre-exponential is the product, $\alpha a_0 v_D$. Since $\alpha$ is a constant and the lattice parameter $a_0$ changes very little, only the Debye frequency $v_D$ could have any real effect. To check this point, the Debye frequency for each alloy at the crossover temperature was calculated from the relation,

$$v_D = \frac{k}{\hbar} \Theta_D,$$

where $\Theta_D$ is the Debye temperature, $h$ is Planck's constant, and $k$ is Boltzmann's constant. This calculation was possible because the composition and temperature dependence of the elastic constants was known, and $\Theta_D$ can be calculated from the elastic constants by (55),

$$\Theta_D^3 = \frac{3.15}{8\pi} \frac{h^3 S}{\rho^{3/2} \nu_a} \frac{1}{(C_{11} - C_{12})^{\frac{1}{2}} (C_{11} + C_{12} + 2C_{44})^{\frac{1}{2}} (C_{44})^{\frac{1}{2}} \nu_a^{\frac{1}{2}}}.$$

It was found that the Debye frequency changed very little, thus confirming that carbon mobility is influenced by an increase in the activation energy term.
The rather large increase in the activation energy is difficult to explain on basis of the relatively small decrease in strain energy. Accordingly, the mobility of carbon, as well as its solubility, must be influenced by the electronic nature of the host matrix.

C. Comments on the Friedel Mechanism

It was found that in all 10 of the alloys examined, the experimental and calculated critical temperatures, $T_a$, agreed very well. These are outlined in the results. The theoretical values were calculated through Equation (13). The implication is that Equation (13) is, perhaps, more general than originally intended. Since it is confined to use at temperatures well below $T_a$, it may be useful for predicting the critical temperature for a variety of thermal barriers to dislocation motion. The experimental evidence of this work points out that in Ni-.2 a/o C, the carbon is fairly mobile, even at low temperatures, yet $T_a$ is predicted exactly. Equation (13), then, is likely to apply in many cases where a discernible, even though small, temperature dependence of the flow stress exists.

Another aspect of Friedel's RSB theory is the prediction of the effective shear stress at $0^\circ K$, $\tau^*$. It was found that where $C < 10^{-4}$ and Equation (16) could be employed, the predictions were very close to the experimental values. However,
where the atomic concentration of solute was greater than $10^{-4}$, $20 \times 10^{-4}$ in the case of this work, the predictions were off. In fact, a $\tau^*$ for $C > 10^{-4}$ was calculated to be lower than for $C < 10^{-4}$. This is just the opposite of what it should be. In the Series II alloys, where the copper concentration was 30 a/o or greater and where the RSB theory applied in all other respects, the predicted $\tau^*$ was too low by a factor of 4. This suggests that some modification of Equation (15) for $\tau^*$ will be necessary.

D. Consideration of Fleischer Hardening

In Table 6, the quantity $\frac{d\tau}{dc}$ is given for 78° and 0°K. Fleischer (42) separates hardening or strengthening into two categories; those termed "gradual" hardeners and those called "rapid" hardeners. For gradual hardening, the increase in shear stress with increase in solute concentration is,

$$ \frac{d\tau}{dc} < 0.1\mu $$

and for rapid hardening it is,

$$ \frac{d\tau}{dc} > 2\mu $$

where $\mu$ is the shear modulus.

It can be seen that none of the alloys tested fall into either one of these groupings, although the tendency is toward gradual hardening especially for nickel. The rate of hardening increases as the copper level is raised and seems to peak
at about 30 a/o Cu after which it declines slowly. According to Fleischer, the rate of hardening is influenced by the tetragonality of the distortions produced by the solute atoms. If this is so, the distortions apparently are more tetragonal in the higher copper alloys. The rate of strengthening in thorium was found to be about 0.50µ (15), practically identical to that found in 30, 45, and 60 a/o Cu alloys. However, it is obvious that carbon even in 30 a/o Cu does not have a great effect on the strengthening process. It could properly be classed as a "moderate" hardener.

E. Strain Aging Experiments

These experiments demonstrated that in a fine-grained Ni-45 a/o Cu alloy, which initially showed a sharp yield drop, the yield drop could not be made to reappear even when aging was done under load at high temperatures and for long times.

The first conclusion is that the initial yield point was not due to interstitials. If it were, a return of the sharp yield drop should have occurred rather easily. This could have been expected because the interstitial content was about $2 \times 10^{-3}$ w/o in this alloy. In iron, Cottrell (56) quotes a range of $10^{-3}$ to $10^{-1}$ as being optimum for an interstitial-induced yield drop. Another fact tending to negate interstitials as the cause of the yield drop is that the interaction energy between a carbon atom and an edge dislocation
in the nickel-copper system is quite low. Based on a hard-
sphere calculation it is only about 0.1 eV. Using a calcu-
lation based on lattice parameter measurements in nickel-
carbon alloys (57), it is even lower, being only about 0.03
eV. This is discussed in Appendix B. Finally, the dependence
of the yield drop on annealing temperature would tend to
preclude atmospheres as the appropriate mechanism.

If the Suzuki mechanism operated to any extent, one would
expect a yield drop to appear after a long-time strain-age.
This, of course, did not occur. A simple calculation shows
why it did not. In the alloy considered, the stacking fault
energy is about 150 ergs/cm$^2$ from the data of Harris, et al.
(11). The resultant equilibrium spacing of the partials
would be about 7.7 b. If a tensile stress of 40 kg/mm$^2$
is applied, which amounts to a shear stress of 12.9 kg/mm$^2$,
the fault separation increases to only 8.1 b. The difference
is not significant. Since 40 kg/mm$^2$ is about the maximum
stress applied to this alloy in testing, it is safe to assume
that no separation occurred. An additional point is that
the diameter of a dislocation core is generally regarded as
being about 10 b. Thus, in the Ni-45 a/o Cu alloy where the
fault width was calculated to be about 8 b, stacking faults
as such do not exist. Accordingly, it would be impossible
for the Suzuki mechanism to operate in this alloy because
there would be no faults into which one of the alloy
components could segregate. The mechanism whereby discontinuous yielding can occur is likely related to dislocation structure in the grain boundaries. A reasonable postulate is that as the isochronal annealing temperature is decreased, the density of dislocations in the region of the grain boundaries is increased. In order for yielding to occur, some of these dislocations must break away from boundaries. The stress to do this is high, but once it occurs, a yield drop is seen. This kind of mechanism could begin to operate in several regions of the specimen at once, and so would spread as the applied load increased. Accordingly, though discontinuous yielding would occur over a range of strain (as observed), it would differ from a Luders type of deformation in that a visible deformation front would be absent. In fact, no Luders front was detected in the experiments. Further, since a significant amount of work hardening took place over the range of discontinuous yielding, the Luders mechanism is precluded.

The observation of an increased magnitude of yield drop and extent of the strain range covered by the yielding as the annealing temperature was decreased simply reflected an increasing density of dislocation tangles in the grain boundaries.
VI. CONCLUSIONS

1. Through extremely rapid quenching-in of carbon, it has been possible to produce mechanical property behavior in a series of nickel-copper-carbon alloys that has some of the characteristics of body-centered cubic structures.

2. Where such behavior occurs, namely in alloys containing 30, 45, and 60 a/o Cu, the Friedel random solute barrier mechanism begins to apply exactly. At the same time, independent experiments show that the carbon atoms are becoming less mobile in the lattice.

3. The mobility of carbon decreases almost linearly with increasing copper content. This was established by the $\sigma_1/\sigma_2$ crossover temperature, and less precisely by the onset of visible serrated flow. Calculations of the activation energy to move a carbon-carbon pair, based on equal mobilities at the different crossover temperatures show an increase from 34,800 calories per mole for nickel (Diamond and Wert's data) to 73,570 calories per mole for Ni-60 a/o Cu. This is too large to attribute to strain energy considerations alone.

4. In addition to lowering the solubility of carbon in the system, additions of copper also decrease the mobility of carbon. This reduced mobility is probably due to some
complex electronic effect, the exact nature of which is still undefined.

5. Results of the present work have been used to rationalize earlier observations in thorium and thorium-carbon alloys.
VII. SUGGESTIONS FOR FURTHER RESEARCH

Internal friction experiments should be carried out on the nickel-copper-carbon system in order to determine in what ways the copper level affects the relaxation processes associated with carbon in the lattice. Also, this would be useful in determining exactly how much carbon actually goes in solution during a fast quench. Such information would be very valuable in alloys containing 60 a/o Cu and higher.

Copper obviously has a significant effect on the mobility of carbon in the matrix. Accordingly, diffusivity studies of carbon as a function of copper content would be informative.

The influence of carbon on the lattice parameters of nickel has been studied (57). An appropriate supplement to this would be to study how the lattice parameters of several nickel-copper alloys change as carbon is added.

Efforts should be directed towards establishing the mechanism or mechanisms whereby the electronic structure of the solvent affects the mobility of the solute species in the nickel-copper-carbon system.
VIII. REFERENCES


47. Suzuki, H., Science Reports of the Research Institute of Tohoku University, A4, 455 (1952).


IX. ACKNOWLEDGMENTS

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Blakemore has attributed the phenomenon of serrated flow in nickel-copper-carbon alloys to the precipitation of $\text{Ni}_3\text{C}$ at mobile dislocations. In effect he presumes that carbon diffuses to the dislocations, and then supersaturates a localized region around the dislocation to the point where precipitation can occur. He believes the precipitate to be $\text{Ni}_3\text{C}$ because in nickel-carbon the serrations disappear at $210^\circ\text{C}$, about the same temperature where carbide instability would cause $\text{Ni}_3\text{C}$ to decompose (58). However, as copper is added to the system, it is observed that the serrations disappear at progressively higher temperatures. This observation would seem to rule out the possibility of a carbide because copper additions promote carbide instability. That is, increasing the copper content decreases the interaction of carbon with nickel and so enhances the tendency toward graphitization. This is clear from the solubility study carried out by Nicholson (43). Accordingly, if carbides controlled the upper critical temperature (see Figure 3), it would be expected to go down as the copper level was raised. Since, in fact, the upper critical temperature does go up, and we know that the tendency for graphitization is increasing, the upper critical is probably controlled by the formation of large graphite particles which are, of course, immobile.
The increase of the lower critical temperature with copper content is explained by Blakemore as a result of decreased carbon mobility. The reduced mobility is attributed to a decrease in elastic misfit (strain energy) between the carbon atom and the matrix. The present work has shown, however, that elastic misfit is not adequate to explain the large increase in activation energy for the diffusion of carbon. More likely, the decreased mobility is associated with an electronic effect, which is acting at the same time to promote graphitization.
XI. APPENDIX B

As noted in the body of this dissertation, hard-sphere calculations were used because no data are presently available on the variation of lattice parameters with carbon content in nickel-copper alloys. However, there is information on lattice dilation of nickel as carbon is added (57). Therefore, it is possible to demonstrate the differences in results between using the hard-sphere approach and the actual change in lattice parameters for calculating the interaction energy between a carbon atom and an edge dislocation. For the hard-sphere model, Equation (28) is used. All it considers is the size difference between the interstitial atom, carbon in this case, and the interstitial site. The maximum binding energy of a carbon atom to a dislocation at a distance of $lb$ comes out to be $-0.129 \text{ eV}$.

If the same quantity is calculated using the experimental lattice parameter change, the following relation is employed (59),

$$W = \frac{4(1+v)}{3(1-v)} \frac{\mu b r_o^3}{L} \sin \theta (\frac{1}{a_o} \cdot \frac{d a_o}{d c})$$

(34)

$L$ is the distance of the solute atom from the dislocation, $r_o$ is the radius of the octahedral site, and $\frac{d a_o}{d c}$ is the change in lattice parameters per atom fraction of carbon. The resulting binding energy comes out as $-0.035 \text{ eV}$, almost a
factor of 4 lower than the previous calculation.

Doing the same kinds of calculations for thorium, the hard sphere model gives an interaction energy of \(-0.0052\) eV. The experimental change in lattice parameters obtained from the work of Michelson and Peterson (16) gives an energy of \(-0.016\) eV. This is an increase of a factor of 3. It is still smaller than the interaction energy in nickel, but only twice as small.

The meaning of these results is that the diameter of the carbon atom in the host matrix is not the diameter associated with the diamond lattice. Based on these calculations, the diameter of the carbon atom in nickel is 1.402Å. In thorium, the effective diameter is 1.760Å. If these diameters are used in a strain-energy calculation, the strain energy in nickel associated with adding carbon is 0.772 eV per atom of nickel. The hard sphere model gave 1.58 eV. In thorium, the strain energy based on the diameter of 1.760Å is 0.429 eV, compared to the previous value of only 0.006 eV.

What this comparison demonstrates is that the hard-sphere approach is probably of value only in a qualitative way and that the numbers obtained can be wrong by as much as 2 orders of magnitude. The weakness is, of course, that the effective diameter of carbon in some foreign matrix is not the same diameter it has in the diamond lattice. These results point out the need to have lattice parameter measurements done in nickel-copper-carbon alloys.