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THE INFLUENCE OF ATOMIC ORDER ON LOW LOAD FRICTION
IN COPPER GOLD (50-50 ALLOY)

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James Albert Cox, III

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THE INFLUENCE OF ATOMIC ORDER ON LOW LOAD FRICTION
IN COPPER GOLD (50-50 ALLOY)

Approved:

Edgar A. Starke, Jr., Chairman

Niels N. Engel

Bruce G. LeFevre

Date approved by Chairman: 11/26/72

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SUMMARY

Low load friction was studied as a function of atomic order in equiatomic CuAu. The coefficient of friction was relatively constant except at approximately $S = 0.8$ where the coefficient of friction exhibited a maximum. A significant observation, which differs from previous work using much larger loads, is that the coefficient of friction is not related to hardness. This maximum coefficient of friction at approximately $S = 0.8$ can be explained in terms of work-hardening characteristics.

Ordered CuAu exhibits a high work-hardening rate because of the increase in antiphase domain boundary area and internal strain which results from perpendicular twin boundaries. The energy of the antiphase domain boundary and the internal strain will increase with increasing degrees of order, thus increasing the work-hardening rate. However, the ordered domain size, which increases as order progresses, will have an opposite effect upon work-hardening. As the domain size increases, the total antiphase domain boundary area will decrease along with the probability of dislocation interaction with antiphase domain boundaries. Thus, as the ordered domain size increases, there will be a tendency for the work-hardening to decrease.

Since work-hardening is controlled by two opposing effects, its maximum will occur at an intermediate degree of order, which in this case is approximately $S = 0.8$.

CHAPTER I

INTRODUCTION

Friction is an extremely complicated process because of the large number of factors which can influence it. Temperature, sliding velocity, pressure, surface contaminants, normal force between surfaces, and varying properties and characteristics of the material or materials involved can all have a marked effect. A small change in any of these may alter the effect of the other factors and thus have a complex and pronounced influence on friction. It is evident that any laboratory investigation will be primarily concerned with attempting to limit and define the number of factors involved and analyze the effect of each.

The present research concerns itself with the effect of atomic ordering on friction. Consideration is given to accompanying factors such as structure, internal strains, work-hardening, yield strength, and hardness, all of which are dependent on the degree of order. Previous investigations of frictional dependence on atomic order have been limited to devices which use large normal forces and thereby complicate the problem by the introduction of surface recrystallization, texturing, and destruction of order by large deformations. This difficulty is eliminated by the use of a new device which accurately measures tangential forces as low as 0.01 dynes. This light load technique may provide a clearer view of the effect of order on the frictional process.

According to modern theory the force of friction arises from two

processes, adhesion and deformation. However, this theory is primarily qualitative, although most investigators attribute the force of friction between metals at relatively large normal forces to adhesion. The present study was primarily concerned with the relationship between order and friction as controlled by deformation or "ploughing." Consequently, an experimental system was chosen to minimize adhesion effects.

CHAPTER II

LITERATURE SURVEY

When two solid surfaces are in contact, any tangential motion of one relative to the other will be opposed by a force developing from a process known as friction. Because solid surfaces are extremely rough on a microscopic scale, the actual area of contact between them will be small.¹ Bowden and Tabor² claim that this force of friction arises primarily from two processes which occur at these small regions of contact. First, strong interfacial adhesion may occur, and the shearing of these interfaces during motion contributes to the force of friction. The second process is deformation, which can be elastic and/or plastic and which may include grooving and ploughing of the surfaces by asperities. The energy spent in these deformations also contributes to friction.

Bowden and Tabor qualify their theory by explaining that the adhesion term is usually the most important, as in the case of metallic contact. However, they point out that the magnitude of the adhesion factor is dependent on the materials in contact. For example, in the case of a gramophone needle sliding over a soft metal surface, the ploughing term may be more important than the adhesion term. Also, for lubricated surfaces the ploughing term may be comparable to the adhesion factor. Numerous workers³⁻⁶ have verified Bowden and Tabor's adhesion theory for metals showing that in general large coefficients of adhesion correspond to large coefficients of friction. Kragelski⁷ disagrees with

Bowden and Tabor on the importance of deformation in friction, even in the case of metals. He asserts, "A more probable assumption will be that friction is caused by bulk deformations and by overcoming the adhesive bonds; the latter increase the resistance to bulk deformations, and this is also affected by work hardening."

According to Bowden and Tabor's theory, friction results from strong adhesion which occurs when surface barriers such as oxides, adsorbed gases, and other contaminants are removed so that the underlying matrixes can make atomically close contact.² To understand how adhesion occurs, let us ignore the presence of surface contaminants and consider two metal surfaces in contact. When one metal is placed on top of another, contact will occur only at the tips of the surface asperities. Any normal load will therefore be borne on these tips. It was Verkhovskii² who first pointed out that, because the load supporting area was small, very high pressures would develop and the contact regions would most likely deform. Thus, as the load is applied, the asperities of the softer material will deform causing an increase in contact area. The downward displacement will bring other asperities into contact causing an additional increase in the contact area. Therefore, when deformation is plastic, the contact area will be proportional to the load.

When actual contact is made between perfectly similar metals, the distance between atoms across the interface is the same order of magnitude as the atomic distance within the matrix. The interfacial atoms cannot distinguish each other from atoms within their own matrix. In effect, the two surfaces have been cold-welded together. Of course, the

actual interface could be related to a grain boundary or at best a twin boundary. For dissimilar metal combinations the same process applies; however, other factors such as solubility must also be considered.⁸

If two surfaces are forced together, it would be expected that the force required to separate them would be proportional to the original force. In actuality, this does not happen. For example, very little adhesion is observed upon separation when a copper specimen is pressed upon a steel specimen. Bowden and Tabor² give two reasons for this. First, oxides or other contaminants prevent strong metallic junctions from forming, and a reduction in adhesion due to contamination has been observed by many early investigators.^{1,2,9} Gilbreath and Sumsion¹⁰ have shown that adhesion decreases with time of exposure to air. They attributed the decrease in adhesion to the increasing amount of oxide.

Bowden and Tabor's second reason for the lack of adhesion is that a great deal of deformation has taken place during the junctions' formation. As a result, work hardening may have occurred, and the junctions will be extremely brittle. This will depend understandably upon the material under study. When the normal force is removed, elastic recovery will lead to upward micro-displacements. As a result, the junctions which formed last will break as the normal force is reduced. Other junctions will break one by one until the load is completely removed. Therefore, removal of the load, which is necessary to measure the force to separate, destroys the adhesion. This explanation has been substantiated by the observation that with ductile materials adhesion is great.^{9,11,12}

Small tangential forces have been shown to increase the area of

contact prior to slip.^{2,11,13-16} Bowden and Young¹⁷ have shown that with the application of a tangential force the contact area between clean metal surfaces in a vacuum can increase to the point at which complete seizure occurs.

The experiments of Courtney-Pratt and Eisner¹⁸ on platinum and steel demonstrated that junction growth for the contaminated surface is essentially the same as junction growth described for clean metals. They explained that, although metallic junctions form and grow, the contaminants present at the interface lower the junction shear strength, and gross seizure will never take place even when metallic contact occurs. When the tangential force becomes greater than the shear strength of the growing metallic junctions, shear takes place and slip will occur. Bowden and Tabor² reported that once slip has begun the sliding surface will climb on the surface film and skid until it slows and penetration and intermetallic welding can take place. This behavior is the intermittent or "stick-slip" motion. It has been observed with some metals that while slip is occurring the electrical resistance rises.¹⁹

Temperature changes may alter material properties and thus cause changes in friction. There is a difference between ambient and contact surface temperatures, the latter being dependent on sliding velocity, load, and the thermal conductivities and temperature of the solids in contact.¹ These surface temperature changes can produce metallurgical phase changes, increased surface activity, ease of deformation, and possibly diffusion within the contact region.²⁰ Buckley²¹ has shown that deformation and heating incurred during sliding caused single and polycrystalline metal surfaces to recrystallize into a textured layer.

Formation of this layer will, of course, depend on the load, sliding velocity, and the metal itself. For a constant sliding velocity the metal with the higher recrystallization temperature will require a heavier load to produce recrystallization. This layer will tend to change the coefficient of friction for single and polycrystalline surfaces, so that at higher loads they will approach a coefficient of friction typical of the textured polycrystalline layer.

Chemically attached films such as oxides have a tendency to prevent metallic contact. If the oxides are thick enough and the loads small, the coefficient of friction will represent a value for pure oxide sliding on itself. As the load increases or the oxide thickness decreases, deformation will begin to occur within the metal matrix, and a different coefficient of friction may result. At some higher load, the oxide will be penetrated, and the coefficient of friction will represent metallic contact.²

Whether or not the oxide will break up is determined by the mechanical properties of the metal and the oxide. Consider Table 1 showing the hardness values of a few metals and their oxides. Also given are the loads at which metallic contact occurs.¹ With aluminum and tin the matrix is extremely soft and the oxide is brittle. At relatively low loads the soft matrix will cease to support the brittle oxide which will crack. Softer copper is approximately the same hardness as the oxide; consequently, it gives support to the oxide, and both matrix and oxide will have some ductility. The matrix support and the ductility of the oxide explain why the metallic contact occurs at a higher load. With chromium both the oxide and the matrix are strong, and penetration will

not occur at loads as high as one thousand grams. Since the thickness of the oxide will determine the load at which metallic contact occurs, the load values given in Table 1 should be considered relative. It has also been noted that with rougher surfaces, the oxide breaks down more readily.

Table 1. Hardness Values of Some Metals and Their Oxides and the Load at Which These Oxides Were Penetrated.

<u>Metal</u>	Hardness-kg./mm. ²		Load at which metallic contact occurs (gm)
	<u>Metal</u>	<u>Oxide</u>	
Tin	5	1650	0.02
Aluminum	15	1800	0.2
Copper	40	130	1.0
Chromium	800	-	1000.0

Wilson²² observed a general decrease in the coefficient of friction with an increase in normal force and attributed it to the presence of an oxide layer. The decrease in the coefficient of friction with increasing load is in violation of Amontons' Laws. (It should be pointed out that the force of friction does increase with load, but this increase is slight in comparison.) Amontons' Laws require a proportional increase.²³ Bowden and Tabor² offered two possible explanations for this behavior. First, at small loads the major part of the deformation is

probably elastic. This type of variation of the coefficient of friction with load has been observed with materials which deform elastically such as diamond and polymeric solids. When deformation between surfaces is elastic, the true area of contact is much less than in the case where plastic flow occurs. In addition, junction growth cannot occur. Therefore, the area of contact and consequently the force of friction do not increase proportionally with load as they do when plastic deformation takes place. Bowden and Tabor¹ noted that plastic deformation must occur before Amontons' Laws will apply.

The second explanation is that sliding on a thin protective film often results in a coefficient of friction which decreases with increasing loads.² This is the principle behind coating a softer metal such as silver on a harder metal such as steel to reduce friction at a previously steel-steel contact area.

A possible limitation of Amontons' Laws exists in two cases: with small contact surfaces or at very high loads. If the load is increased, the real area of contact might grow until it is equal to the apparent area of contact. The real area of contact will then remain relatively constant with increasing loads, thus leading to a violation of Amontons' Laws.

There have been relatively few studies of friction on single crystals. Although such studies cannot directly explain polycrystalline behavior, they help to isolate the effects of the structure. Bowden and Tabor² pointed out that friction is always lowest on close-packed planes. In fact, friction with single crystals seems to follow the crystallographic slip behavior. Buckley²⁴ has studied the effects of orientation

upon adhesion and friction. His results confirm that the coefficient of adhesion is lowest on the closest packed planes. Adhesion on these planes seems to be inversely proportional to their Young's Modulus. Buckley explains this in terms of the area of contact. As the Young's Modulus increases, so does the resistance to deformation. For a given load the (111) plane, with its higher Young's Modulus, will deform less resulting in less contact area. Another possibility is that elastic recovery, which is proportional to the Young's Modulus, will destroy the junctions. Whatever the reason, deformation does vary with orientation. Buckley also points out that the surface energy of each crystallographic plane is proportional to adhesion. This agrees with Rabinowicz's ideas.²⁵ Buckley also measured the adhesion and friction for the (100), (110), and (111) planes contacting the (100) plane. The results showed that matched (100) planes have higher adhesion than unmatched planes.²⁴

Bowden and Tabor² point out that the hardness of metals has little effect on friction. They explain that if soft metals are in contact the area of contact will be large, but the shear strength will be small. Conversely, for hard metals in contact under the same load, the area of contact will be small, but its shear strength will be large. In this way they account for the similarity in the force of friction observed with hard and soft metals.¹ Skiorski,^{26,27} however, has shown that adhesion and consequently friction do have a dependence on hardness for materials with similar crystal structures.

Another important feature of hardness which may influence low load friction is an apparent difference between surface hardness and bulk hardness. Microhardness measurements with very low loads always

give higher values than measurements made with larger loads.²⁸ At very light loads the size of the indentation is so small that the deformed metal around it no longer contains the same concentration of dislocations as the bulk matrix. Therefore, the metal will appear harder.

Sikorski²⁶ has shown that the purity of copper has a noted effect on adhesion. For copper and gold alloys Buckley²⁹ explained the dependence of adhesion upon purity in terms of its changing ability to adsorb contaminants. It should be noted that purity has numerous other effects on friction, because it can alter hardness, ductility, crystal structure, thermal conductivity, the ability to form oxides, etc.

It has been pointed out that ductility, thermal conductivity, ability to form oxides and adsorb gases, crystal structure, lattice parameter, Young's Modulus, hardness composition, purity, shear strength, work-hardening characteristics, and surface energy all depend on the material or materials in contact and will therefore influence the frictional process. The types of frictional studies conducted in the past have not been conducive to the separation of structural and/or physical parameters which influence frictional behavior. Correlations have been made with various parameters; but these parameters have often been altered by changing either the chemical composition or the temperature of the alloy under study, thereby introducing new variables. Hardness has been extensively used in correlations with friction, but this parameter depends on both the yield strength and work-hardening performance of a material and therefore cannot be used in any theoretical treatment. This is the reason that confusion exists between the conclusions of Bowden and Tabor and those of Sikorski concerning the effects of

hardness on friction.

The ideal approach for studying the basic phenomena which govern the friction of materials would be to use an alloy in which the structural characteristics such as crystal system and physical properties could be varied independently of alloy composition and temperature. Only in such a system could the many variables be isolated for correlation with friction. Fortunately, such systems are available in alloys which undergo an order-disorder transformation.

When two metals are alloyed together, their atoms are normally distributed randomly on the lattice sites. However, there may be more unlike or like bonds between atoms than required for perfect randomness; this situation is known as short-range order.³⁰ In some alloys strong atomic preference may lead to intermetallic compounds. Within these compounds each type of atom will occupy a specific lattice site at all temperatures below the melting point. A limited number of alloys of specific composition can exhibit a random atomic arrangement at high temperatures, while at lower temperatures their structure is identical to an intermetallic compound and is said to possess long-range order. The degree of atomic order has been described by Bragg and Williams by a long-range order parameter, S , defined as

$$S = \frac{r_A - F_A}{1 - F_A}$$

where r_A is the fraction of A sites occupied by A atoms in the AB binary alloy.³¹ F_A is the atomic fraction of A atoms in the alloy. Therefore, for a disordered alloy, $S = 0$, and for complete order, $S = 1$.

There are two processes by which order is obtained.³² The first is a nucleation and growth mechanism, by which highly ordered particles nucleate and grow in the disordered matrix. The second is a homogeneous process, by which the number of unlike bonds increase in the matrix. In addition, ordering can result in a change in crystal structure. In the case of CuAu the disordered structure is face-centered cubic, while the ordered structure is face-centered tetragonal.³¹ Cu_3Au is face-centered cubic in both the ordered and the disordered conditions.

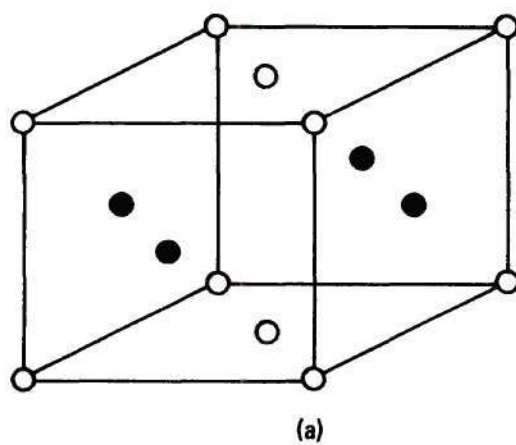
Many workers have observed that a maximum in yield stress in certain alloys occurred at some stage of the ordering process between $S = 0$ and $S = 1$.³²⁻³⁴ In addition, numerous theories have been advanced to explain the actual dislocation mechanisms responsible for the increased strength of partially ordered matrixes. Fisher³⁵ has proposed a mechanism to explain strengthening in short-range ordered materials. Marcinkowski and Miller,³³ Stoloff and Davies,³² Flinn,³⁶ and Cahn³⁷ offered theories to explain strengthening in long-range ordering alloys. Vidoz and Brown³⁸ have stated that work-hardening in ordered alloys results from the production of superjogs during deformation. As deformation continues, both the superjog density increase and the creation of a trailing tube of antiphase domain boundary with superdislocation motion contribute to work-hardening.

It has already been explained that ordering in CuAu is accompanied by a change in crystal structure. Actually, the process is even more complicated than was indicated, because two ordered crystal structures are possible depending on the ordering temperature. Above 410°C the crystal structure of CuAu is disordered face-centered cubic. By a slow

cooling from high temperatures or by isothermal ordering below 380°C , an ordered tetragonal structure known as CuAuI will form (Figure 1A). The gold and copper atoms are arranged in separate layers which are the (002) planes, and c/a is 0.93.

Isothermal ordering between 420°C and 380°C will result in orthorhombic CuAu, known as CuAuII (Figure 1B). The CuAuII cell is made up of ten tetragonal cells like CuAuI placed side by side. However, five of them appear to have resulted from translation vectors of $c/2$ and $a/2$. The structure, therefore, consists of a copper layer, five atoms in length, followed by a layer of gold of the same length all on the (002) plane. Each of the ten cells is not tetragonal but orthorhombic because of distortion. That is, the length of the cell is not $10a$ but $10.02a$ and $c/a = 0.92$.

Kuczynski, et al^{39,40} using x-ray diffraction techniques, showed that ordering in CuAu takes place by a nucleation and growth mechanism. Hirabayashi, et al^{41,42} said that ordering begins as coherent nuclei which consist of (101) ordered platelets. As these platelets grow, their difference in atomic volume creates elastic strains. At some point in the ordering process, the strain precipitates twinning. Hirabayashi and Weissman said that twinning occurs in two stages, microtwinning and macrotwinning. They attributed both to the elastic strains. Arunachalam and Cahn,³⁰ however, felt that the microtwinning resulted from the interaction of ordered regions with different c -axes during growth. They felt that, if microtwinning had resulted from a stress relief mechanism, they would have observed a drop in hardness at this stage of ordering.



○ Cu
● Au

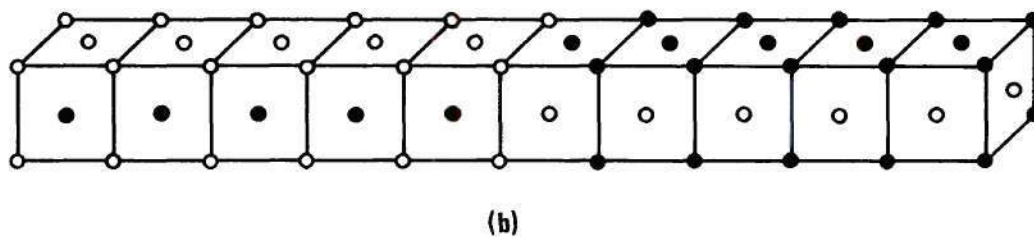


Figure 1. Ordered Structures in CuAu: (a) CuAuI (below 380°C) and (b) CuAuII (380°C - 410°C).

Harker⁴³ observed that as ordering progressed the microstructure of polycrystalline CuAu showed a "rippled" surface appearance within the grains which increased with increasing order. Arunachalam and Cahn³⁰ observed this same appearance and distinguished twin marking within the grains the amount of which increased with ordering. They also noted that, as ordering progressed, the grain boundaries thickened, and they suggested that this effect resulted from grain boundary sliding. The strain created by the disorder-order transformation and subsequent twinning in CuAu single crystals often results in distortion. In polycrystalline specimens stress induced boundary migration and grain boundary fracture can also occur to reduce the strain.

Some interesting aspects of deformation were pointed out by Arunachalam and Cahn.³⁰ In the CuAuI both unit dislocations and superlattice dislocations can glide due to the unique structure. A unit dislocation with a Burgers vector of $\frac{1}{2}\langle 110 \rangle$ will not destroy order as it glides, while those with Burgers vectors of $\frac{1}{2}\langle 101 \rangle$ and $\frac{1}{2}\langle 011 \rangle$ will. In addition, since twinning on (111) type planes is possible, only the partial dislocations involved with this deformation can have the Burgers vector $\frac{1}{6}\langle 112 \rangle$, because they preserve order.

Two early investigations of the mechanical properties of CuAu were made by Nowack⁴³ and Harker⁴⁴ and consisted of measurements of hardness of initially disordered CuAu as a function of ordering time. Both Nowack and Harker found an increase in hardness due to ordering. For temperatures above 200°C, Nowack found that a maximum hardness was followed by a softening at longer annealing times. Harker, however, found no pronounced maximum in his hardness measurements. Hirabayashi, et al

attributed the initial increase in hardness, which occurred upon ordering, to coherency strains between ordered nuclei and the disordered matrix. The decrease, observed by Nowack, at longer ordering time was explained in terms of stress relief mechanisms, twinning, and recrystallization.

Two recent investigations were made of the effect of the ordering process in CuAu upon hardness. Arunachalam and Cahn³⁰ have studied this effect at 150°C, 240°C, and 340°C using both quenched and cold-worked samples. At 150°C the quenched CuAu sample showed an increase in hardness with increasing time up to one thousand minutes. At the higher temperatures all samples showed an immediate increase in hardness, and the rate of this increase became larger at the higher ordering temperatures. All samples showed a decrease in hardness at greater annealing times with the exception of the quenched sample ordering at 150°C. Thus, a fully ordered sample may have various hardnesses depending upon the temperature at which it was ordered. Arunachalam and Cahn explained that at higher ordering temperatures, the rate of ordering is so high that rapid stress relief mechanisms, particularly twinning, occur. At lower ordering temperatures, approximately 150°C, the rate of ordering and the coherency strain production is too slow for twinning to occur. This explains the decrease in hardness with the higher ordering temperatures.

Because hardness measurements really measure the effect of two factors, work-hardening and flow stress, Arunachalam and Cahn studied the effect of ordering at 150°C on flow stress. They found an increase in yield stress with ordering and attributed it to the changes in dislocation characteristics. However, they concluded that work-hardening had

the greatest effect upon the observed hardness changes.

Horne and Starke⁴⁵ have also studied the effect of ordering on hardness in CuAu. They determined the effect of ordering time at 200°C. There are two important differences between their results and the results obtained by Arunachalam and Cahn. The former conducted their ageing for a greater length of time. At 200°C, the maximum hardness was reached just below one thousand minutes. As ageing continued the hardness decreased. Secondly, Horne and Starke observed a minimum in hardness after approximately two minutes of ordering at 200°C.

Buckley⁴⁶ studied the effects of atomic order on friction with alloys of copper containing ten, twenty-five, and fifty atomic percent gold. The latter two alloys, Cu₃Au and CuAu, are ordering alloys. Friction measurements were made in a vacuum with the alloy sliding on 440-C stainless steel at various velocities. A constant load of 1,000 gm. was used in all cases. The 90%Cu-10%Au exhibited a constant coefficient of friction for all sliding velocities below 600 cm./sec. At higher sliding velocities a decrease in the coefficient of friction was observed. This decrease in the coefficient of friction above 600 cm./sec. was attributed to the decrease in strength due to the increasing interface temperatures. The CuAu alloy was tested in the same manner. However, in this case two samples were used: one disordered and one ordered. The disordered CuAu alloys were heated to 450°C and water quenched. The ordered structures were obtained by annealing at 375°C for 48 hours. Samples were checked by x-ray diffraction for long-range order. The disordered sample exhibited a constant coefficient of friction, 1.2, up to sliding speeds of 750 cm./sec. A much lower coefficient

of friction, 0.35, was observed with the ordered sample when the velocity was below 375 cm./sec. Above this speed the coefficient increased to a maximum of about 0.7. Buckley attributed this to increased interface temperature which caused the material to disorder. The coefficient never reached the value of the disordered sample, 1.2, and it was assumed that only partial disorder had occurred. After the speed reached 450, the coefficient of friction started to drop off slowly. Again, Buckley attributed this to the thermal reduction of mechanical properties at the interfaces.

When 440-C stainless steel slid on copper-gold alloys, it was observed that copper-gold adhered to the stainless steel surface. This resulted in the formation of a thin film of copper gold shielding the stainless steel. In order to determine of the order-disorder transformation would be observed without the film, Buckley measured the coefficient of friction for ordered CuAu sliding on itself at a constant velocity of 198 cm./sec. An increase in friction was observed as the temperature increased. The Cu_3Au data exhibited similar behavior.

Using a twist compression bonding technique Bailey and Sikorski²⁷ studied the effect of atomic ordering upon adhesion with CuAu. The maximum and medium coefficients of adhesion, made under normal loads of 200 gm., along with the hardness of each condition were determined. The ordered structure was harder and had the smaller coefficient of friction. Bailey and Sikorski concluded that the hardness, which was governed by the ordering process, was the determining factor in adhesion.

Previous studies of the effect of atomic order on friction have not attempted to determine the effect of intermediate degrees of order,

the corresponding long-range order parameters, and/or antiphase domain size on friction. In addition, the large normal forces used in the experiments introduced other parameters, such as recrystallization and texturing, which have been shown to have noted effects upon friction.

CHAPTER III

EXPERIMENTAL PROCEDURE

The CuAu alloy (M.P. = 890°C) was prepared by induction melting high purity copper and gold, encapsulated in vycor tubing in a vacuum of 10^{-6} torr, to form CuAu. The sample was furnace cooled to 800°C and quenched in ice water. It was cleaned by swabbing it with a solution consisting of five volumes of glacial acetic acid, one volume of orthophosphoric acid, one volume of hydrochloric acid, and three volumes of nitric acid. The sample was then rinsed and placed in a reagent consisting of equal volumes of solutions containing 20 grams of KCN in 100 ml. of distilled water and 20 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 100 ml. of distilled water, respectively. After removal the sample was rinsed, dried, and encapsulated as before in vycor tubing in a vacuum of 10^{-6} torr.

A single crystal was grown using the Bridgman technique with a Lindberg Hevi-Duty resistance furnace and then quenched from 800°C in ice water. Small sections were cut from both ends of the sample, by spark discharge, to obtain flat cross sections. In order to remove deformed material, these surfaces were mechanically polished through 0.3 micron alumina, rinsed in acetone and distilled water, and chemically polished. Subsequent x-ray Laue back-reflection patterns from different areas of both ends of the sample confirmed that it was a single crystal. In addition, the removed end pieces were mechanically polished through 0.3 micron grit and etched with aqua regia. A microscopic examination revealed no grain boundaries. The CuAu single crystal was cleaned,

encapsulated in vycor tubing under a vacuum of 10^{-6} torr, and homogenized at 850°C for nine days.

After homogenization the sample was oriented using x-ray techniques and sectioned parallel to the (110) plane within an accuracy of ± 2 degrees. All cutting was done on a spark discharge machine, and each wafer was approximately 0.11 cm. thick. After sectioning the large surfaces of each wafer were mechanically polished through 0.3 micron grit, rinsed, and chemically polished to remove the surface material disturbed by the spark machining.

Each wafer was rinsed in acetone and distilled water respectively, dried, and encapsulated in a separate vycor tube in a vacuum of 10^{-6} torr. The first sample was then placed in the Lindberg Hevi-Duty resistance furnace and maintained at 800°C . After twenty-three hours the temperature was lowered to 600°C , and after one hour the sample was quenched to room temperature. This process was repeated for each of the samples. To remove the possibility of oxidation during quenching, the wafers were carefully mechanically polished through 0.3 micron grit, chemically polished, rinsed, and then dried. In order to verify that the CuAu single crystals were disordered, each was scanned using a G.E. XRD-6 Diffractometer by techniques described elsewhere.⁴⁷ In each case the fundamental (220) reflection was present while the superlattice (110) reflection was negligible in comparison.

Ageing was conducted by immersing each wafer, held in a vycor holder, in boiling dimethylformamide, $\text{HCON}(\text{CH}_3)_2$. The setup was arranged so that the temperature in the location of the sample was fairly constant at 150°C . The times for the ageing of the samples were predicted

from the theory devised by Ling and Starke.⁴⁸ If the degree of order as a function of ordering time at a particular temperature is known, the relationship between the degree of order and ordering time at another temperature can be determined using the Ling-Starke equation given below.

$$\frac{-\ln(1 - S_{T_1})}{-\ln(1 - S_{T_2})} = \frac{e^{-Q_{ot}/RT_1}}{e^{-Q_{ot}/RT_2}}$$

S_{T_1} = the long-range order parameter known to result from ordering at temperature T_1 for a particular time.

S_{T_2} = the long-range order parameter which will result from ordering at another temperature T_2 for the same time.

Q_{ot} = the activation energy of ordering.

R = 1.98726 Cal./degree Mole.

T_1 = the temperature (K) at which the degree of order is known for a particular ordering time.

T_2 = the temperature (K) at which the degree of order is to be determined for the same ordering time.

The degree of order was determined for each wafer using techniques described by Ling.⁴⁷ Basically, this consisted of the comparison of the fundamental and superlattice reflections as shown in the following equation:

$$S = \frac{E_s/I_s}{E_f/I_f}$$

where E_s and I_s are the estimated superlattice intensity and the measured

superlattice intensity respectively. E_f is the estimated fundamental intensity, and I_f is the measured fundamental intensity. One of the CuAu wafers became seriously warped during ordering; although the exact degree of order for this sample could not be determined, it was approximately $S = 0.8$.

The average ordered domain size was determined using the Scherrer equation³¹ employing the method described by Stoloff and Davies⁴⁹ for removal of instrumental and strain broadening. The final form of the equation was

$$t_D = \frac{0.9\lambda}{\beta \cos \theta_S}$$

where t_D is the average ordered domain size, λ is the x-ray wavelength (1.54Å for CuK_α radiation), $\beta = \sqrt{B^2 - (B^*_{220})^2}$, B^*_{220} is the corrected breadth of the (220) peak at one half maximum intensity in the as quenched condition, B is the breadth of the given superlattice peak at one half maximum intensity, and θ_S is the observed Bragg angle of the superlattice peak.

The value of B^*_{220} was determined in the following way. The average particle size of the sample was determined using Scherrer's equation:

$$t = \frac{0.9\lambda}{B_{220} \cos \theta_{220}}$$

where t is the average particle size, B_{220} is the observed breadth of the (220) peak at one half maximum intensity in the as quenched condition,

θ_{220} is the observed Bragg angle of the (220) peak in the as quenched condition.

The corrected value, B^*_{220} , was determined using Scherrer's equation:

$$B^*_{220} = \frac{0.9\lambda}{t \cos \theta_s} .$$

Friction measurements were made using an instrument which was developed for measuring small friction forces and which has been described elsewhere.^{50,51} The friction couple consisted of one of the (110) surfaces of the CuAu single crystals, varying only in the degree of order, and a Realist stereo diamond stylus. Diamond was chosen so that adhesion effects would be minimized. The radius of the tip of the diamond stylus was measured on a metallograph and found to be 0.016 cm. The same diamond was used for all samples. All friction runs were made in the close-packed direction, and the velocity was always 0.001 cm./sec. Before each set of friction runs, the wafer was washed in acetone and methyl alcohol respectively to remove surface films and then carefully dried. The normal forces used were as follows: 5 mg., 10 mg., 15 mg., 25 mg., 50 mg., 75 mg., and 100 mg.

After measuring the frictional forces of each CuAu single crystal wafer in contact with the diamond stylus, the hardness of each sample was measured using a Tukon hardness tester with a diamond indenter and a load of 500 grams. A minimum of thirty indentations was made on each sample, and their average was taken.

CHAPTER IV

RESULTS

Low load friction was studied as a function of the degree of atomic order in CuAu. Friction measurements were made with the (110) surface of single crystal wafers of CuAu in sliding contact with a diamond stylus. To eliminate geometric differences the same diamond stylus was used for all wafers, and the sliding direction in relation to the diamond was always constant. All sliding was in the close-packed direction on the (110) surface of the CuAu single crystal. The only parameter which varied was the long-range order parameter of each crystal. Tables 2 and 3 list the average force of friction and the average coefficient of friction for each sample with each normal force.

Figure 2 shows the change in the average coefficient of friction with the change in the long-range order parameter for each normal force used. In addition, the Knoop hardness values are shown as a function of the degree of long-range order. The CuAu single crystal wafers had long-range order parameters of $S = 0.0$, $S = 0.4$, $S = 0.6$, $S \approx 0.8$, and $S = 1.0$. With each normal force a new path on the (110) CuAu surface was used. In each case the average coefficient of friction showed a slight maximum at $S = 0.4$ and a pronounced maximum at $S \approx 0.8$. It should be noted that the average coefficient of friction for the disordered condition, $S = 0.0$, was less than for the ordered condition, $S = 1.0$, and the lowest occurred at $S = 0.6$. However, these differences between $S = 0.0$,

Table 2. Average Measured Force of Friction Data.

Load	Average Force of Friction MG				
	S = 0	S = 0.4	S = 0.6	S = 0.8	S = 1.0
5MG	1.22	1.79	1.08	3.77	1.77
10MG	2.32	3.08	2.13	6.54	3.01
15MG	3.14	4.24	2.77	9.96	3.81
25MG	4.82	5.93	4.37	13.60	6.04
50MG	9.32	10.58	8.99	22.60	10.34
75MG	14.16	14.81	12.61	25.04	15.00
100MG	19.16	20.08	17.31	32.65	20.14

Table 3. Average Coefficient of Friction Data.

Load	Average Coefficient of Friction MG				
	S = 0	S = 0.4	S = 0.6	S = 0.8	S = 1.0
5MG	.247	.358	.230	.754	.354
10MG	.252	.316	.213	.653	.301
15MG	.217	.283	.185	.664	.254
25MG	.209	.237	.175	.544	.241
50MG	.201	.212	.180	.452	.207
75MG	.193	.197	.168	.334	.200
100MG	.195	.200	.173	.327	.201

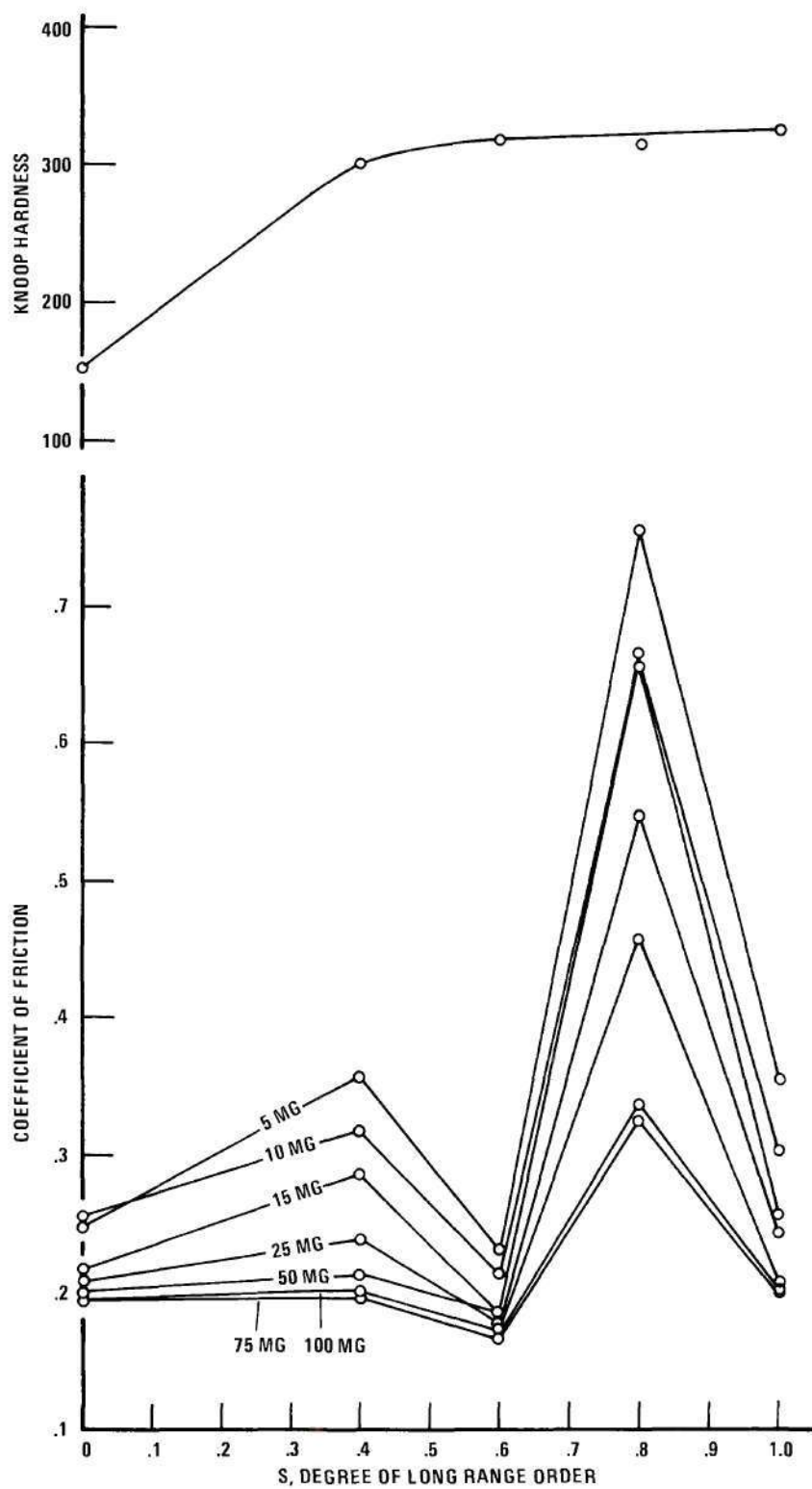


Figure 2. Knoop Hardness and Coefficient of Friction Versus Long-Range Order Parameter for CuAu.

$S = 0.4$, $S = 0.6$, and $S = 1.0$ are minute in comparison to the maximum at $S \approx 0.8$.

The coefficient of friction for each wafer is shown as a function of the normal force in Figure 3. For each wafer there is a general decrease in the coefficient of friction with increasing normal load. This decrease is most pronounced when $S \approx 0.8$. At higher loads the average coefficient of friction for each degree of order seems to become somewhat constant. The spread in the average coefficients of friction for the various degrees of order is greatest at five milligrams normal load and decreases as the load increases.

Table 4 gives the sample number, the degree of long-range order, the Knoop hardness, the average ordered domain size, and some comparison data on yield strength.³⁰

Metallographic examination showed that the polished (110) wafer surfaces developed a rippled appearance as observed by Harker.⁴⁴ This condition increased for samples with increased ageing time. Arunachalam and Cahn³⁰ attributed this effect to the deformation by twinning which occurs in CuAu upon ordering. It is interesting to note that the samples which were aged to obtain degrees of order of $S \approx 0.8$ and higher experienced warping. The amount of warping was highest for the sample for which $S \approx 0.8$. This and the rippled surface appearance seemed to be directly related to the ordering process.

A metallographic examination of the diamond stylus at 500X and 1000X magnification after the friction runs revealed no particles of CuAu, a finding which supports the original concept that little or no adhesion would occur between diamond and CuAu. Each wafer was also

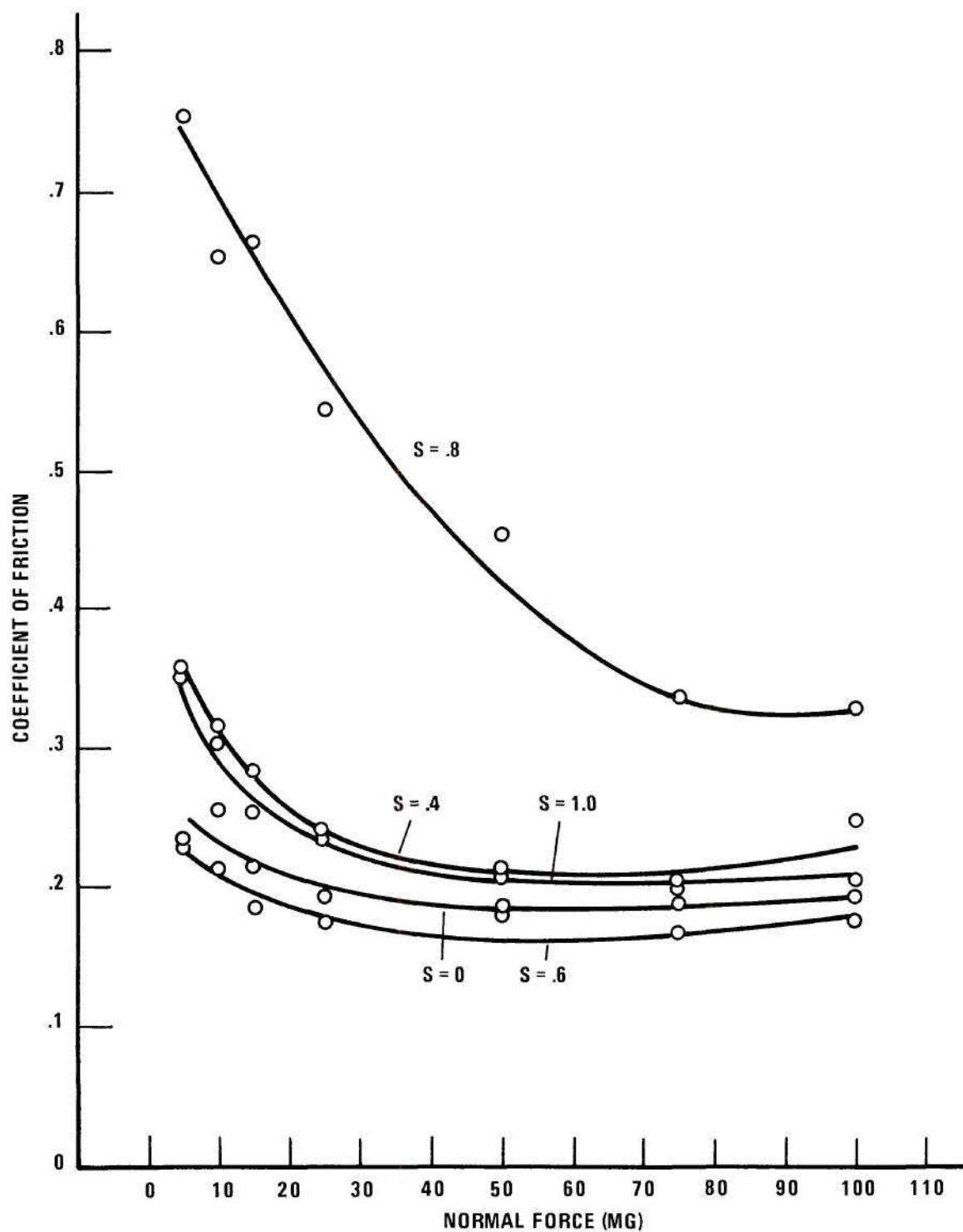


Figure 3. The Coefficient of Friction Versus the Normal Applied Force for Each Degree of Order Studied.

Table 4. Summary Data.

Sample Number	Ageing Time (Minutes) at 150°C	Degree of Order	Hardness Knoop Tukon 500 gm.20X	Yield Strength from Arunachalam and Cahn ³⁰	Average Ordered Domain Size
2	0	$S \approx 0$	154	21 kg/mm ²	0Å
5	350	$S \approx 0.4$	300	41 kg/mm ²	40Å
7	1710	$S \approx 0.6$	319	42 kg/mm ²	60Å
1	1800	$S \approx 0.8$	314		
8	3400	$S \approx 1.0$	321		130Å

examined optically after the friction runs, and no evidence of the diamond stylus path was observed, indicating that the deformation of at least the surface layer was primarily elastic.

CHAPTER V

DISCUSSION OF RESULTS

Friction is the result of two processes, adhesion and ploughing. In this experiment the forces of friction were measured between a diamond stylus and CuAu. Because of the lack of compatibility between these two structures² and the presence of adsorbed vapors from the air,²⁹ it is felt that adhesion was probably negligible and that the ploughing process was the primary cause of the force of friction for these experiments.

By using the degree of order as the parameter with which friction is varied, the change in friction may be related to structural characteristics, such as crystal system and physical properties, independent of any effects of temperature and composition. The slow speed of the sliding stylus and the light loads also eliminated any additional effects of temperature which might have led to recrystallization and texturing.²¹ The direction of sliding was always in the close-packed direction to eliminate other crystallographic factors.

Figure 3 shows that the coefficient of friction is decreasing with increasing load for each degree of order. This is similar to Wilson's²² observations while studying the friction of steel. He attributed the decreasing coefficient of friction to the presence of an oxide layer. Although CuAu probably has an oxide layer, a more logical explanation is related to the type of deformation at the interface.² At small loads the major part of the deformation is probably elastic, and the true area of

contact is much smaller than in the case where plastic flow occurs. In addition, junction growth cannot occur. Thus, the true area of contact and, consequently, the force of friction do not increase proportionally with load as they do when plastic deformation takes place. However, after a normal force of 70 mg is reached the coefficient of friction for all degrees of order remains essentially constant with load. The different variation of coefficient of friction with load for the various degrees of order may be related to changes in Young's modulus with order. Young's modulus increases with the formation of ordered CuAuI.⁵²

Another possible answer can be found in the configuration of the small spherical diamond stylus. Only a portion of the stylus contacted the CuAu at the lighter loads. As the load is increased, the area of contact cannot increase proportionally due to the spherical configuration.

A possible oxide could have affected the force of friction. Since gold does not have an oxide, it was assumed that the only possible oxide was copper oxide. Bowden and Tabor give the Vickers Hardness for copper oxide as 130 kg./mm.² Arunachalam and Cahn³⁰ give the Vickers Hardness range of CuAu as 150-320 kg./mm.² depending on the degree of order. Since the matrix was harder, the oxide would resist cracking. In addition, the oxide could cause a change in the force of friction which was not proportional to the normal force.

A significant result of this experiment is the lack of a correlation between hardness and the average coefficient of friction which is in agreement with the conclusions of Bowden and Tabor.² The greatest difference in hardness is between the fully ordered sample and the disordered sample. However, the difference between the average coefficients

of friction for these two degrees of order is small. The maximum change in the friction coefficients occurs at $S \approx 0.8$; but the hardness of CuAu is relatively constant from $S = 0.6$ to $S = 1.0$. Arunachalam and Cahn³⁰ have shown that ordering in CuAu has a greater effect on the work-hardening rate than on the yield stress. The increase in yield stress on ordering was found to be less than the increase in hardness. Since large deformations are introduced during hardness measurements, the hardness of a metal should be dependent on the work-hardening rate.

The high coefficients of friction, which occurred at $S = 0.8$, can be explained in terms of the work-hardening characteristics of the alloy. Ordered CuAu exhibits a high work-hardening rate because of the increase in antiphase domain boundary area and internal strains produced during ordering and difficulty of dynamic recovery by cross slip. When the adjacent ordered domains in CuAu have orthogonal tetragonal c axes, a misfit lattice strain will exist at the antiphase domain boundary. These boundaries are normally called perpendicular twin boundaries. A dislocation or a superdislocation intersecting such an antiphase domain boundary will require an additional force to continue motion due to the creation of a jog in the antiphase domain boundary. This additional boundary will also have a misfit strain energy associated with it. Deformation will be accompanied by the production of new antiphase domain boundary and internal strain, which in turn will lead to work-hardening.

The energy of the antiphase domain boundary and the internal strain will increase with increasing degrees of order. Since work-hardening is dependent on these two factors, it will also be expected to increase with increasing degrees of order. However, the ordered domain size, which

increases as order progresses, will also have an effect upon work-hardening. As the domain size increases, the total antiphase domain boundary area will decrease, along with the probability of dislocation interaction with antiphase domain boundaries. Therefore, as the ordered domain increases, there will be a tendency for the work-hardening to decrease.

Work-hardening is controlled by two opposing effects, one causing it to increase as order progresses and the other causing it to decrease as the structure orders. A maximum in work-hardening will therefore occur at an intermediate degree of order which in this case is $S = 0.8$. When the diamond stylus ploughs across the CuAu surface, resistance will come from matrix deformation ahead of the stylus. Work-hardening of the matrix will offer resistance to stylus motion and will offer maximum resistance when the work-hardening rate is maximum at $S = 0.8$.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Low load friction between CuAu of varying degrees of atomic order and diamond is independent of the hardness of the CuAu.
2. A maximum coefficient of friction occurs at an intermediate degree of order, approximately $S = 0.8$.
3. This maximum coefficient of friction can be explained in terms of the work-hardening characteristics.
4. When CuAu single crystal wafers, cut parallel to the (110) plane, are ordered at 150°C ., maximum warping occurs at approximately $S = 0.8$.

Recommendations

1. A study of low load friction should be initiated using CuAu of varying degrees of atomic order with a surface with which the adhesion portion of friction could be significant. Comparison of this data with the present work might lead to an understanding of the interdependence of adhesion and ploughing.
2. A more detailed investigation of warping in CuAu as ordering progresses at 150°C should be undertaken. Knowledge of the exact degree of order at which warping is a maximum could further the understanding of ordering in CuAu.
3. Measurements on other crystallographic planes should be made.

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