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Studies on the Nature of Passivity in "K" monel

By

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Abstract

In order to ascertain the influence of age hardening upon the nature of passivity of "K" monel, passivating phenomena of the alloys in quenched state and also in aged state are measured. Age hardening is rather favourable to corrosion resistance of "K" monel in early stages of ageing. To make sure the mechanism of this behavior, results are discussed from the view point of slip resistance.

§ 1. Introduction

Because they have high corrosion resistance and high strength, the useful application of precipitation hardening stainless steel, age hardening nickel alloys and many other corrosion resisting alloys which have precipitation hardening property, is becoming increasingly important in structure or appliances that are used under severe conditions. However, there is little information on the effect of the age hardening treatment on resistance to corrosion of solid solution alloys.

An interesting theoretical attempt has been made by Evans¹⁾ to solve this problem. He considered that when a metal is corroded, the atoms have to be pulled apart from one another, therefore, the increase of work done of inter atomic separation or resistance to gliding will be favourable to corrosion resistance of the alloy. From this assumption, he calculated the work down which is required to cause the slip in disordered single crystal from the mutual potential between the atoms. Evans' result shows good agreement with experimental data.

In the case of precipitation hardening alloys, especially in the early stages of segregation, this assumption may be expected to be reasonable. Although this consideration is supported by the earlier measurements of Fetz²⁾ on the copper-nickel-tin bronzes, from this consideration, it is extremely difficult to explain the behavior of some

alloys, in which the corrosion velocity is controlled rather by the nature of protective films than by the unpolarized potential. Nevertheless, observation of passivity in carbon steel by F. Fenwick²⁾ and a recent report⁴⁾ on the passivation of 25 pct. chromium steel by auther and associate indicate that the increased hardness of the alloy will be favourable to chemical stability. Therefore, another mechanism must be considered for an explanation of these facts.

The present paper reports some measurements on the passivity of "K" monel in the solution treated condition and also after ageing. In order to make clear the relationship between the age hardening and nature of passivity, the results are discussed.

§ 2. On the passivity in "K" monel under constant current density

1. Material.

"K" monel ingot is made by melting electrolytic copper and copper-aluminium mother alloy (50:50) in a Tammann furnace. The ingot is reduced to strip about 1 mm thick by room-temperature swaging and rolling. The composition of this material is given in Table 1.

TABLE 1. Composition of the sample.

Ni	Al	Cu
65.56	3.4	remainder

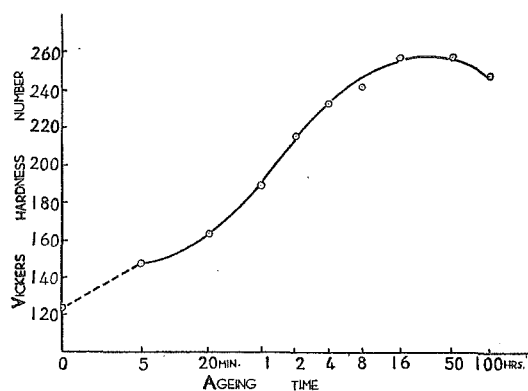


Fig. 1. Age hardening of the "K" monel.

2. Heat-treatment.

The specimens are homogenized at 1000°C for 3 hr. in vacuum furnace and after a solution-treatment of 30 min. at 870°C, specimens are quenched in water. Ageing treatment is carried out in vacuum furnace at 590°C for various ageing times. The specimens are always air-cooled after ageing.

Variation of hardness with the ageing time is shown in Fig. 1. Peak hardness is reached after ageing for 16 hr. but after ageing for 100 hr., specimen reaches a condition of over-ageing. No visible precipitation has been observed in the micro-structures of the specimens even after ageing for 100 hr. by etching with Carapella's reagent (FeCl_3 , 5g, $\text{HCl}_{(\text{conc})}$ 2 cc. and Ethyl alcohol 99 cc.).

3. Measurement of current density vs. potential curves.

Five pct. sulphuric acid solution is used as electrolyte and netted platinum electrode is used as cathode. Constant current is supplied from a circuit with a high voltage battery and a high resistance. The temperature is maintained at 20°C during the measurement and the electrolyte is stirred by a magnetic stirrer. The surface of the electrode is pickled by the Carapella's reagent during 30 sec. for removal of the polished layer and then the electrode is set in the measuring cell. A certain current is applied and the potential is measured after 30 sec. and then a higher current is applied and the operation repeated until passivation occurs.

Experimental results are shown in Fig. 2. The following relation is found between anodic polarization π and current density i .

$$\pi = a + b \log i.$$

In this equation, a and b are constant. From this result, approximate critical current density for passivation can be presumed. In the case of solution treatment specimen, the critical current density is 20~40 mA/cm², whereas it falls at about 10~20 mA/cm² in the aged specimens.

4. Amount of coulombs/cm² needed for passivation of "K" monel.

A relay is placed in circuit with high resistance and high voltage, in order to switch in the constant current, at the suitable instant. On the other hand, potential is measured by oscillograph and bulb-potentiometer.

Circuit of the bulb-potentiometer is shown in Fig. 3. In this diagram, M denotes a millivoltmeter and an oscillograph which are

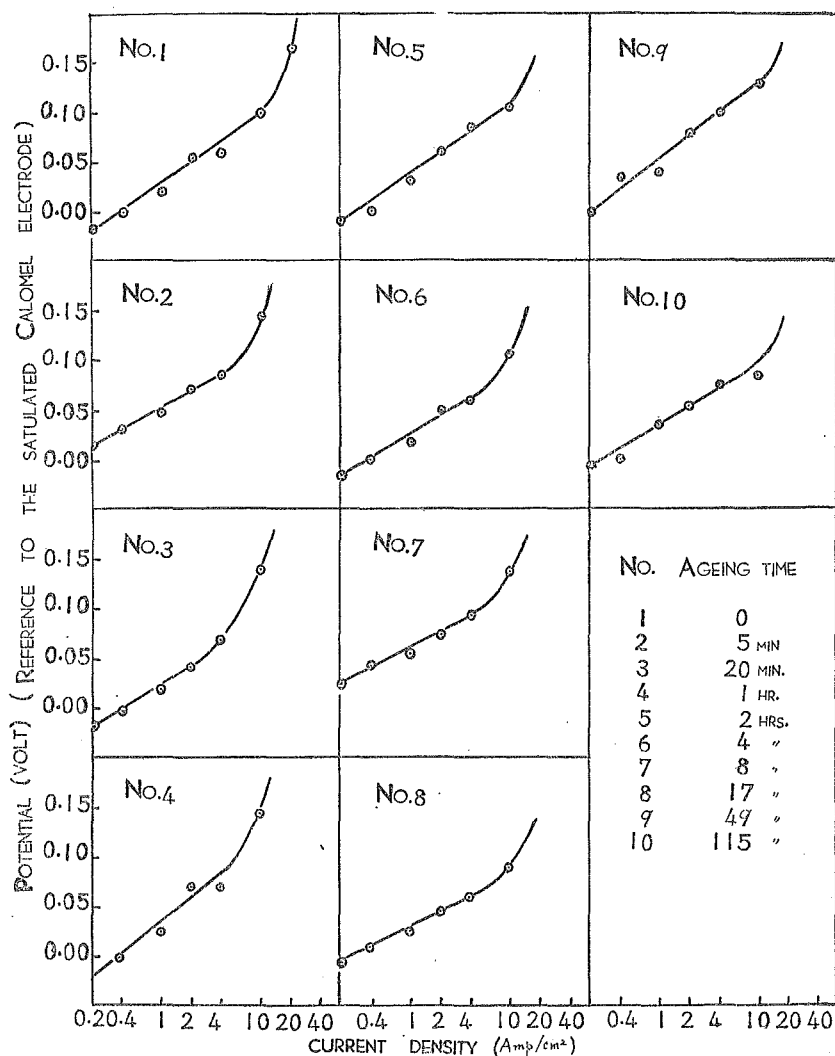
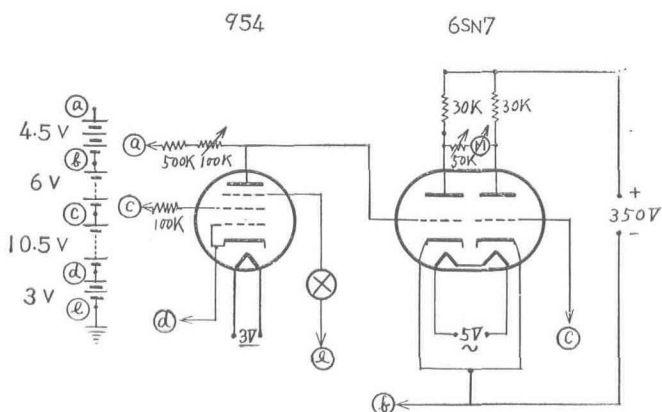
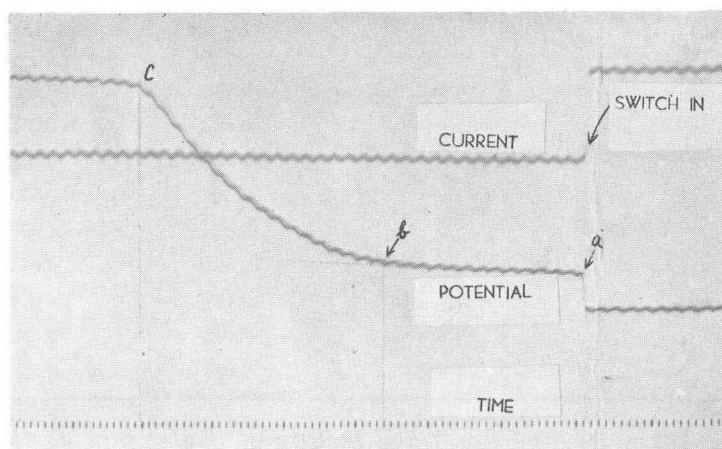


Fig. 2. Anodic polarization of the "K" monel in 5% H_2SO_4 .

connected in series. X is the electrolytic cell; one terminal is connected to the specimen and others to the calomel reference electrode. The bulb 954 is made to be operated in low voltage, therefore the grid current is extremely small⁹. Before the measurement, X is shortend and zero point is corrected. Then the sensibility is adjusted by use of cadomium standard cell.



An example of the oscillogram is shown in Photo. 1. Current, potential and time are recorded simultaneously. As is shown in Photo. 1, when the current is switched on, the potential is suddenly increased. (a). This jump of potential is attributed to the charge of the electric double layer between the sample and electrolyte. Thereafter, linear slow increase of potential is observed. (a~b). Dissolution of alloy starts at a, consequently the slow increase of potential until b is attributed to the change of concentration polarization upon the electrode surface. Then later potential rises rapidly from b to c at which oxygen evolution occurs. Therefore, oxide film will probably spread over the electrode surface at this point.



Following relation has been found by Frank for passivating of iron.

$$(i - i_0) \cdot t_p = \text{const.} \quad (1)$$

where i is anodic current density, i_0 is current density below which passivating is not possible, t_p is the time between the onset of the passivating current and the sudden rise of the potential indicating the formation of the passive oxide layer. This equation is confirmed by Olivier⁶⁾ for passivating of iron-chromium alloys. In order to test whether or not the equation is applicable to the passivating of "K" monel, the following experiment was carried out

A. Influence of the holding time.

When the current is cut off after the electrode has passivated, the potential decreases and soon the potential returns to the initial values in active state. The time between the cut off of the passivation current and the once more switching in of the current to produce the passive state is named holding time.

From the cut off of the passivating current to the instant the potential returns to the initial values in active state, 10 sec.~3 min. are required. Therefore, in order to test the influence of the holding time upon the amount of coulombs/cm² needed for passivation and reproducibility of experimental results, the electrode is held in various times about 5 min. Results are given in Table 2.

TABLE 2. Influence of the holding time upon the passivation time

No.	holding time	current density	passivation time	
			a~c	b~c
1	5 min.	135.6 mA/cm ²	0.022 sec.	0.022 sec.
2	10	"	0.052	0.052
3	15	"	0.073	0.073
4	20	"	0.085	0.072
5	30	"	0.090	0.076
6	40	"	0.094	0.075
7	60	"	0.103	0.074
8	15	135.4	0.102	0.075
9	30	139.0	0.088	0.073

In this Table, No. 1~No. 6 are results of one run of experiments; during these measurements, electrolyte is not renewed and electrode

is not repolished. No. 7 and No. 8 are obtained results from the same sample but with freshly prepared electrolyte and repolished electrode. Further, the same experiments are carried out by use of the current density of 180 mA/cm² and 100 mA/cm².

From these results it is concluded that the time from the onset of the passivating current required to complete the passive state (a~c in Fig. 2 or t_p in equation (1)), is increased nearly by the increase of holding time and reproducibility of the result is not obtained. That is to say, equation (1) is not applicable to the passivity of "K" monel.

When the holding time is less than 15 min., the time from the start of the formation of oxide film required to complete the passive film (b~c in Fig. 2), depends upon the holding time, similarly as above. In these regions, a~b change is almost nonrecognizable and steep ascent is observed immediately after the change of the electric double layer, in the oscillogram. However when the holding time is not less than 15 min., a~b change appears clearly in the oscillogram. In these regions, b~c becomes constant in spite of the change of holding time and good reproducibility is obtained.

B. Effect of the temperature.

Effect of the temperature upon the time between a and c, and also between b and c is measured. The results which obtained for various temperature, are shown in Table 3.

TABLE 3. Influence of the temperature upon the passivation time

No.	temperature	passivation time	
		a~c	b~c
1	5.0 °C	0.065 sec.	0.060 sec.
2	13.0	0.067	0.062
3	24.8	0.256	0.087
4	31.5	0.168	0.100
5	39.0	>1.0	—

In this experiment, 30 min. is selected for the holding time and 140 mA/cm² is used as the current density. Effect of the temperature upon the passivation time is relatively large. Especially the time between a and c, is greatly increased by increase of temperature.

Solubility of the salts which are produced by dissolution of the electrode, and diffusion velocity of the salt from the electrode surface, will be increased by rise of temperature. Therefore, it is probable that the time until the salt saturates on the electrode surface, is very much increased by increase of temperature.

C. Influence of other factors.

Influence of the agitation velocity upon the passivation time is not large. When the agitation is not applied, the passivation time is considerably decreased. However, appreciable change upon the passivation time is not observed by the variation of velocity of the stirrer. Especially, influence of the velocity of stirrer upon the time between b and c is of the order of the experimental error.

Influence of nickel ion (Ni^{++}) and copper ion (Cu^{++}) concentrations in the electrolyte is tested; Experiments are carried out when 6.7 g/l ~ 26 g/l of nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and 6.7 g/l ~ 26 g/l of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) are added into the electrolyte and other conditions are maintained constant. Unexpectedly, the addition of nickel sulphate extremely increases the time required. It is considered that this result is attributable to the chlorine ion which is detected as an impurity in nickel sulphate salt. In the case of the addition of copper sulphate, no appreciable influence is observed.

D. Influence of the age hardening upon the number of equivalents necessary to passivate the alloys.

From the above experiments, under the following conditions, the passivation times are measured on the aged "K" monel; temperature is maintained at 20°C, holding time is selected as 20 min., electrolyte is stirred by the magnetic stirrer during the experiment, and 5% sulphuric acid is used as the electrolyte. Results are given in Table 4.

The amount of coulombs/cm² needed for passivation is calculated by the product of the current density and passivating time. The relation between the ageing time and the number of equivalents necessary for passivation of samples is given in Fig. 4.

As is shown in Fig. 4, at first the number of equivalents necessary to passivate is decreased, and then is increased by lengthening of the ageing time. From a comparison of Fig. 1 and Fig. 4, the ageing time, in which the number of equivalents necessary to passivate is minimized, is shorter than the ageing time, to be required to give the maximum hardness.

TABLE 4. The number of equivalents necessary for passivation

Sample No.	Current density mA/cm ²	Passivation time		Number of equivalents (milli-coulombs/cm ²)		
		b~c sec	a~c sec	b~c	mean	a~c
1	176.0	0.110	0.130	19.4	21.4	22.9
	118.0	0.185	0.305	21.8		26.0
	66.0	0.350	0.930	23.1		61.4
2	178.0	0.110	0.135	19.6	20.7	24.0
	118.0	0.163	0.267	19.2		31.5
	60.0	0.390	1.155	23.4		69.3
3	183.0	0.090	0.115	16.5	18.7	21.0
	118.0	0.168	0.210	19.8		24.8
	60.0	0.330	0.627	19.8		37.6
4	180.0	0.100	0.127	18.0	18.6	22.9
	120.0	0.160	0.203	19.2		24.4
	62.0	0.300	0.550	18.6		34.1
5	178.0	0.083	0.095	14.8	15.1	17.1
	119.0	0.127	0.156	15.1		18.6
	58.4	0.262	0.415	15.3		24.2
6	181.0	0.083	0.100	15.0	15.7	18.1
	119.6	0.128	0.168	15.3		20.1
	60.0	0.280	0.450	16.8		27.0
7	179.0	0.083	0.113	14.9	14.2	20.2
	119.0	0.130	0.185	15.6		22.2
	60.0	0.202	0.438	12.1		26.3
8	179.0	0.083	0.108	14.9	16.3	19.3
	119.6	0.132	0.193	15.8		23.0
	58.6	0.312	0.537	18.3		31.5
9	179.6	0.105	0.125	18.9	18.6	22.5
	119.8	0.142	0.203	17.0		24.3
	57.6	0.343	0.615	19.8		35.4
10	182.2	0.085	0.102	15.5	16.9	18.6
	119.8	0.155	0.183	18.6		21.9
	60.0	0.275	0.763	16.5		45.8

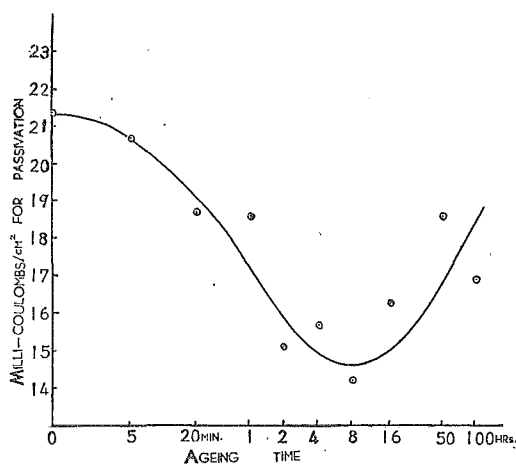


Fig. 4. The number of equivalents necessary for passivation.

§ 3. On the passivity in "K" monel under constant potential

The nature of passivity in "K" monel is studied by the measurements of current density under constant potential. Applied potential is measured by the direct reading type bulb potentiometer and controlled by the variable resistance. Pure nickel plate is used as cathode whilst other conditions in the measurement are the same as in the above experiments. An example of anodic polarization curve obtained in this experiment is shown in Fig. 5.

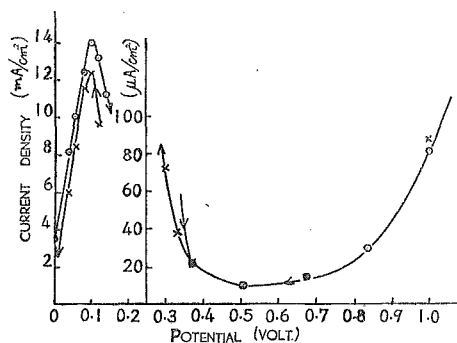


Fig. 5. Anodic polarization curve.

1. Current density which is necessary to maintain the passive state.

After the specimen has been passivated, the potential is decreased

to a certain voltage and the current is measured after the potential is maintained the voltage during one minute. Thereafter, the potential is decreased to the next voltage and the operation is repeated. As is shown in Fig. 5, the current decreases rapidly to about 0.8 volt and then it reaches minimum value at about 0.5 volt. After that, the current increases and at last the specimen returns to the active state. The relation between the minimum current density which is gained by this experiment and ageing time, is shown in Fig. 6.

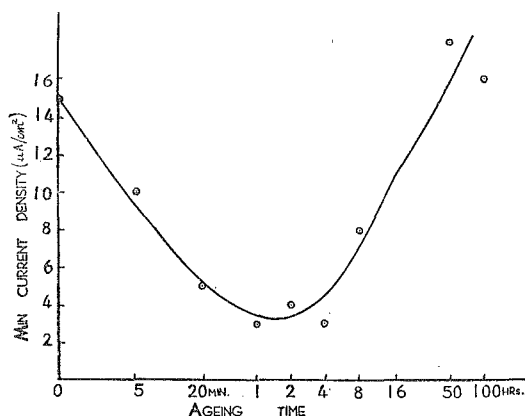


Fig. 6. Minimum current density.

This current density is considered to be the minimum current density which is necessary to maintain the specimen in the passive state. This current density decreases with increase of ageing time and reaches the minimum more rapidly than the specimen reaches the maximum hardness.

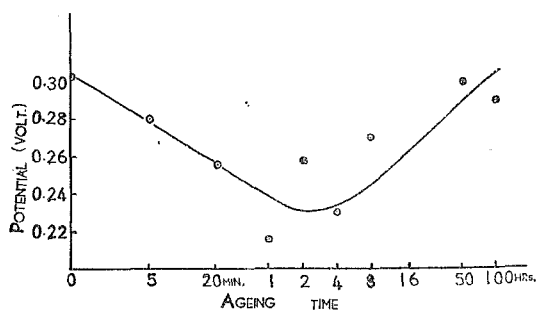


Fig. 7. The potential in which the specimen returns to the active state.

2. The potential in which the specimen returns to the active state.

The potential in which the specimen returns to the active state is plotted against the ageing time in Fig. 7.

Observed values are scattered in this figure, therefore clear results are not obtained. But it seems that the same tendency as in Fig. 6 may be observed from this figure.

§ 4. Considerations

Evans has point out that the increase in hardness is favourable to the corrosion resistance of a solid solution alloy, especially in the early stage of age hardening. The author has observed that even in the alloy, in which the corrosion velocity is controlled by the nature of passivity, Evans' expectation may be applicable. Moreover, from this study it is observed that in the early stage, the age hardening is favourable to the passivity of "K" monel.

According to the dislocation theory, increase of hardness of the alloy is explained as being due to movement of the dislocation in the alloy becoming more difficult. Therefore, when the formation of superlattice or precipitation occurs resulting from the heat treatment of solid solution alloy, the dislocation may be stabilized and larger external force is required to move the dislocation. Consequently, increase in hardness is observed in general.

When the solid solution alloy is corroded, the preferential dissolution may be caused to occur from the part where the dislocation meets the surface of alloy. This is true because energy which is necessary to pull apart the atom from a perfect crystal is greater than that from an imperfect portion. Consequently, good correspondence is observed between the pit and the dislocation and especially one to one correspondence has been observed⁷⁾ between the pit which is formed in early stage and the dislocation in single crystal.

In the case of the alloy, in which oxide film or protective film is not formed, corrosion is spread over the crystal and is observed as a uniform corrosion. However, in the case of the alloy in which the oxide film is formed, corrosion may proceed as a local corrosion or pit corrosion. When the passive film breaks up for any certain cause and the metal comes in contact immediately with the corrosive reagent in that portion, this portion acts as the anode of a local cell against the other where the oxide film is covered. Consequently, this portion is

strongly attacked and a pit is formed.

In the present investigation, density of dislocation may be almost the same in all samples whether the ageing time is long or short. This is true because, excess dislocation may be diminished during the ageing treatment and air cooling treatment. It is difficult to explain the stabilization of the oxide film which is accompanied by the hardness increase of "K" monel by means of the difference of the density of dislocation.

During the microscopic observation of dislocation upon evaporated silver, Forty and Frank⁹ have found a slip which occurs naturally on the specimen without any external stress. Of course, these slips are almost all elementary slips. They considered that these slips may be results of internal stress due to the diffusion of small quantities of an impurity.

If the elementary slip is able to occur even as a result of such small internal stress, it will be reasonable to consider that an elementary slip may have occurred in the present electrode, because the present electrode has internal stress caused by air cooling and lattice distortion caused by precipitation and moreover the pit corrosion has occurred at the surface of the electrode. Under these experimental conditions, the internal stress in the specimen should be great enough to produce an elementary slip.

If the elementary slip occurs in the alloy which is covered with a thin protective film, micro-crack will be produced in that passive film and specimen makes contact immediately with electrolyte at this portion. Accordingly, dissolution of the alloy occurs and a pit is formed. Subsequently, other slip in succession may be induced.

When specimens have almost the same extent of internal stress, movement of dislocation or formation of slip becomes more difficult as a result of the increase of hardness of alloy. Therefore, from the above assumption, so far as the increase in hardness is not accompanied by an increase of dislocation density of alloy and in the case only when the oxide film is very thin (about a few atomic layers), it is easily presumed that the increase in hardness which occurs for example, by age hardening will stabilize the passivity of the alloy.

When the precipitation has proceeded further, although the hardness is increased continuously, alloy becomes to be considered as a two phase alloy. Therefore the passivity of alloy becomes unstable above a certain ageing time.

Although this assumption shows good agreement with the experimental results, it must be confirmed by further studies to ascertain whether or not the elementary slip occurs just as thought.

§ 5. Conclusion

The nature of passivity of "K" monel in sulphuric acid is measured and following results are obtained. Current density-potential curve of "K" monel in 5% sulphuric acid is measured under constant current density and a linear relation is found between anodic polarization and logarithm of current density in all samples. Approximate critical current density for passivation of quenched sample is 20~40 mA/cm², whereas that of aged sample is about 10~20 mA/cm². Influence of holding time, temperature, agitation velocity and addition of salts to the electrolyte upon the number of equivalents necessary to passivate the "K" monel are measured. It is concluded that Frank's equation is not applicable to the passivity of "K" monel and when the holding time is not less than 15 min., reliable data can be obtained. The number of equivalents necessary to passivate vs. ageing time curve is minimized at a certain ageing time. Minimum current density which is necessary to maintain the passive state is measured by the constant potential method. The current density is decreased by increase of ageing time and reaches the minimum more rapidly than the specimen reaches the maximum hardness. The same tendency is shown in the potential in which the specimen returns to the active state.

The influence of age hardening upon the nature of passivity of "K" monel is discussed from the standpoint of dislocation theory. Mechanism of stabilization of passivity is considered by assumption of occurrence of elementary slip.

Acknowledgments

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