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A NEW CORROSION RESISTANT ALUMINUM PRODUCT

By E. H. Dix, Jr.  
Metallurgist, Research Bureau  
Aluminum Company of America

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A NEW CORROSION RESISTANT ALUMINUM PRODUCT.\*

By E. H. Dix, Jr.,  
Metallurgist, Research Bureau,  
Aluminum Company of America.

The corrosion of aluminum alloys has been the cause of much concern to those interested in the successful application of metal in airplane and airship construction. Within the past few years it has been made the subject of much discussion, both constructive and destructive. Examples of corrosion occurring under unusual and severe conditions have been cited as reasons why aluminum alloys should not be used even under relatively protected conditions.

As a result of this situation the whole subject has received careful consideration in many quarters and much experimental work is now in progress. Although much information has been obtained concerning the nature of the corrosion attack and protective coatings, yet very little has hitherto been accomplished towards making major improvements in the corrosion resistance of the strong alloys themselves. One conclusion is outstanding, namely, that while in comparison with steel aluminum is highly corrosion resistant, or "rust proof," yet for

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satisfactory service, thin sections of the strong aluminum alloys of to-day require some protection, especially when subjected to severe conditions such as salt water or mist. It is worthy of note, however, that under normal atmospheric conditions unprotected strong aluminum alloys are giving very satisfactory service, the radiator shells used in a popular automobile being one excellent and familiar example.

In aircraft, however, where so much depends upon the absolute reliability of every unit, it is essential that the structural parts have a maximum of resistance to deterioration under service conditions. Aircraft, especially seaplanes, are often subjected to atmospheres which have a very corrosive effect on most metals. Hence, it is now the practice to protect all metal parts by paint or varnish. If this is carefully done the aluminum alloys suffer little deterioration, but there is always the possibility of a careless job where parts are hurriedly put together without first having a shop coat, and so the joints are not properly protected. Such conditions may easily escape subsequent inspection, and corrosion and failure may result. Blisters, checking, and abrasion may further cause the failure of the protective coating. Under severe conditions as in the case of the pontoons of seaplanes, the life of the best protective paints is short and the structure must be frequently reconditioned. Here again there is always a chance of overlooking inaccessible places.

Anodic protective films have received considerable attention lately and several methods of producing them are said to be practicable and to give good protection. However, the process is rather costly and it is difficult to treat large assemblies. If single parts are treated the coating may be injured in assembling, since all of these films are very thin and easily abraded. The Bureau of Standards have previously reported that pure aluminum applied by the metal spray process stands up in strong corrosion accelerants which caused failure of the other coatings tested.

During the past four years the research laboratories of the Aluminum Company of America have been very active in studying the corrosion resistance of aluminum and its alloys. Attention has been concentrated on the effect of corrosion as measured by the mechanical properties (strength and elongation), rather than by the loss or gain in weight. The most serious type of corrosion, intergranular penetration, causes relatively little change in weight but a pronounced loss in ductility appears at an early stage and is followed by a loss of strength. The corroding medium most generally used in our laboratories is a fine mist from a 20 per cent salt solution. Work has also been in progress on other methods of accelerating corrosion such as repeated immersion in various solutions. A particularly active medium used by the Bureau of Standards is a 6 per cent salt solution containing 10 per cent by volume of commer-

cial 3 per cent hydrogen peroxide. This solution seems to be very useful in determining whether or not an alloy is susceptible to intergranular penetration. A period of 48 hours in this test appears to have a corrosive action equivalent to from 8 to 12 weeks in the salt spray tank.

It should be clearly recognized that even the mildest accelerated corrosion test is far more severe than the worst conditions ever encountered in actual service, and moreover, that accelerated tests at best are very unsatisfactory and the results are often inconsistent and confusing. It is particularly dangerous to draw too definite conclusions from a single series of tests or to assume that comparisons made under one set of conditions will hold under an entirely different set.

One of the most difficult questions to answer is "What is the relative corrosion resistance of the various aluminum alloys?" unless the particular corroding medium is specified. A slightly salty mist is one of the most severe conditions which aluminum alloys are likely to encounter under normal service in structural parts and hence the salt spray is a logical medium for accelerated corrosion tests.

The character and extent of the attack have been carefully studied microscopically. These studies have led to the very important conclusions that commercially pure aluminum and at least one alloy containing about 1-1/4 per cent manganese are immune from intergranular penetration by corrosion. In con-

trast the strong alloys in which the high strength and hardness are obtained by a heat treatment involving the precipitation of certain of the constituents, such as  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$  are more likely to suffer this type of attack. The extent of the damage (loss in tensile strength and elongation) cannot be determined by inspection of the surface, and therefore the structure may be greatly weakened and embrittled without giving visible warning.

Not all lots of strong alloys corrode in this manner and it is known that certain compositions are more susceptible than others. However, the corrosion attack which proceeds by pitting alone may have just as severe an effect in reducing the tensile strength and elongation. Some of the other factors influencing the corrosion resistance have been determined, but none that has more than a minor effect. The difference between the corrosion resistance of the best lot of the present type of strong alloy which has ever been tested in our laboratories and the "run-of-mill" material is not sufficient to promise that its use would result in a marked increase in life of a structural part under ordinary conditions of aircraft service.

It is the purpose of this paper to describe a new corrosion-resistant aluminum product which is markedly superior to the present strong alloys. Its use should result in greatly increased life of a structural part. This product, designated

"Alclad," has been in the course of development by the Research and Technical Departments of the Aluminum Company of America for some time. It is now felt that sufficient progress has been made to assure its commercial production.

Corrosion studies show that with a few possible exceptions the corrosion resistance of pure aluminum is lowered by the addition of alloying elements. Samples of pure aluminum sheet (99.95 per cent) 1/8 inch thick have been in the salt spray tank for a period of 2-1/2 years, with relatively little attack. A notable exception to the statement made above is the addition of manganese, which may even improve the resistance to certain corrosive agencies. However, manganese improves the strength and hardness to a minor extent only and when such other elements as copper and magnesium are added in sufficient quantity to give maximum strength and hardness the corrosion resistance is considerably lowered. A product combining the corrosion resistance of pure metal at the surface and the strength of the strong alloy underneath would seem to be ideal to meet the service conditions imposed by aircraft. Some six years ago in our laboratories an attempt was made to produce a composite sheet by rolling a strong alloy between sheets of aluminum, but the results were not very promising. Now, however, this combination has been successfully achieved in "Alclad."

A clear conception of the nature of the product may be ob-

tained by reference to the micrographs of Figs. 1 and 2. The former shows at a magnification of 50 diameters the full cross-section of a piece of 14 gauge "Alclad" 17ST sheet, and the latter a portion of the same area at higher magnification. Our symbol "17ST" denotes a heat-treated aluminum-copper-manganese-magnesium alloy. The section has been deeply etched to reveal the grain structure of the pure metal surface, which is clearly shown at the top and bottom of Fig. 1. The alloy core has been over-etched and stained so that its structure is obscured. An intermediate diffusion zone will be observed between the alloy and the pure aluminum. It is due to the diffusion of some of the alloying elements (copper and probably the magnesium-silicon constituent  $Mg_2Si$ ) from the alloy into the pure metal during fabrication and heat-treatment. This diffusion occurs only at high temperatures and results in a gradual transition from the strong alloy to the pure metal.

A study of this diffusion of the soluble constituents of the alloy base into the pure metal surface is of particular interest. It has shown conclusively the thorough character of the union between the alloy and the pure metal. The rapidity with which this diffusion takes place at heat-treating temperatures may be illustrated by the results obtained in some experiments which were performed on "Alclad" 17S foil 0.003 inch thick. Pieces of this foil were heated for different periods of time at  $515^{\circ}C$  in an air chamber submerged in a nitrate bath.



Fig. 3 shows the cross section of a composite sample made up from ten pieces of this foil which had been quenched after heating for periods of 1, 5, 10, 15, and 30 minutes, respectively, reading from left to right of micrograph, there being two samples for each heating period. One minute was not sufficient to cause solution of the constituents even in the alloy base, so that the two left-hand specimens retain the characteristic appearance of hard-rolled material. Five minutes, however, has been sufficient to cause the solution of most of the constituents in the alloy and has caused diffusion into the pure metal which at the grain boundaries extends entirely through the surface. Ten minutes as shown by the fifth and sixth specimens from the left has caused further diffusion. Fifteen minutes as shown by the seventh and eighth specimens has caused diffusion to the surface over practically the entire area. This is, of course, also true in the case of the two right-hand specimens, which were heated for thirty minutes.

Figs. 4 and 5 show the diffusion in four different gauges of thin sheet, which have been heat-treated in a nitrate bath at  $510^{\circ}\text{C}$  for ten minutes and then water-quenched. The right-hand portion of Fig. 4 shows the full cross section of 28 gauge (0.013 inch) sheet. The diffusion has extended half-way through the pure metal, except at the grain boundaries where it has penetrated all the way. The left of the micrograph shows the full cross sections of two pieces of thirty-four gauge (0.006

inch) sheet. The diffusion in this case has extended to the surface over the whole area. Fig. 5 shows another piece of 28 gauge sheet between a piece of 21 gauge (0.028 inch) sheet on the right and a piece of 22 gauge (0.025 inch) sheet on the left. The former was rolled from 0.102 inch thick sheet with one intermediate annealing and the latter from the same lot of 0.102 inch thick sheet without intermediate annealing. The piece of 28 gauge sheet shown in Fig. 4 was rolled directly from 0.102 inch sheet, whereas the same gauge sheet in Fig. 5 had two intermediate annealings during the rolling from 0.102 inch. These intermediate annealings do not seem to have affected the amount of diffusion.

Figs. 6 and 7 give an interesting comparison between the relative thicknesses of pure metal surface and base metal core in 14 gauge (0.064 inch) sheet and in the same sheet rolled to foil of a thickness of 0.0017 inch. Fig. 6 shows three pieces of the 0.064 inch sheet magnified 15 times, and Fig. 7 shows three pieces of the 0.0017 inch foil magnified 500 times. With these relative magnifications the sheets in both pictures seem to have about the same thickness, and the relative proportion of pure metal to the alloy core will be seen to be the same. The foil has not been heat-treated and undissolved particles of constituent are clearly visible.

In the first corrosion test on "Alclad" 17ST sheet it was shown not only that the pure metal surface was free from attack,

but also that the alloy exposed along the edge of the sheet was unattacked. Fig. 8 shows the extent of the pitting along the edge of normal 17ST 14 gauge sheet due to continuous exposure for eight weeks to the spray of a 20 per cent salt solution. Fig. 9 shows a similar edge of "Alclad" 17ST sheet which was exposed in the same spray tank for the same period. The pure metal surface is shown at the right and the exposed edge (uncovered alloy) at the top. It is seen that no attack occurred. A similar effect was found in the alternate immersion test, employing the salt-hydrogen peroxide solution. Fig. 10 shows the exposed edge of 7/16 inch 20 gauge 17ST channel after 48 hours' exposure. Severe intergranular attack has taken place. A similar edge of "Alclad" 17ST channel of the same size is shown, after the same exposure, in Fig. 11. No attack has taken place at this edge although the alloy was exposed. It was further found that even though the surface was removed from comparatively large areas the exposed alloy was not attacked.

Thus it appeared that the pure metal was exercising a protective effect on exposed areas of the alloy. Measurements of the potential between strips of pure metal and of 17ST immersed in a beaker of salt solution showed that the pure metal was electronegative to the alloy, and hence could be expected to exercise an electrolytic protection. That is, it appears that because of the higher solution potential of the pure metal as compared to the alloy a protective effect is exercised much

like the protective effect of zinc on galvanized iron articles. The effective radius of this protection has not been determined.

This relation is in marked contrast to that between nickel and aluminum, for in the case of nickel plating if even a small pinhole allows the aluminum to become exposed, then the contact between the aluminum and the nickel causes greatly accelerated corrosion of the aluminum. In active solutions such as the salt-hydrogen peroxide, the pure aluminum on the surface of "Alclad" 17ST slowly dissolves along the edge of the sheet where the alloy is exposed, but the alloy remains intact.

The salt spray corrosion tests to date include the exposure of samples of "Alclad" 17ST with a surface of 99.95 per cent pure aluminum for a period of 24 weeks and the exposure of similar samples with a surface of 99.75 per cent pure aluminum for a period of 8 weeks. Many other combinations have been made up and are being tested, but the tests will not be completed for several months. These tests include those of 17ST protected by aluminum of different grades of purity, namely, 99.0, 99.5, 99.75, 99.85, 99.95 per cent, also heat-treated aluminum-copper-manganese and aluminum-magnesium-silicon alloys protected with several different grades of aluminum, as well as 17ST protected by the aluminum-manganese alloy and by the aluminum-magnesium-silicon alloy. Even after 24 weeks' exposure the changes in tensile strength and elongation of the "Alclad" 17ST when any occurred, were so small as to be well within the limits of ex-

perimental error. Some surface corrosion of the pure metal had taken place, but was not sufficient to cause the specimens to break through those areas. All of the fractures were clean and unmarked by corrosion. Samples of "Alclad" 17ST which had intentionally been deeply scratched or deformed show no corrosion after four months' exposure.

In the lighter gauges, approaching the thickness of foil, the diffusion of copper into the pure aluminum surface must be considered. In this case unless the ratio of the thickness of the pure aluminum layer to that of the alloy core is greatly increased, the pure metal layer is extremely thin and diffusion proceeds to the surface. The corrosion resistance of the product is still excellent as compared with that of normal 17ST.

In order to study the effect of a small amount of copper in solution in pure aluminum a series of alloys was made up from 99.95 per cent pure aluminum containing copper up to 3/4 per cent. Specimens of 23 gauge (0.025 inch) sheet of these alloys were heated at 530° C. for 52 hours to promote uniform diffusion of the copper, quenched and reheated for 2½ hours at 510 to 530° C. in a nitrate bath and again quenched. They were then corroded for five days by alternate immersion in the salt-hydrogen peroxide solution. The results indicate that under the conditions of this test copper as high as 3/4 per cent does not greatly lower the corrosion-resistance of the pure aluminum.

The soft, ductile metal on the surface of "Alclad" metal seems to aid in difficult forming operations. Some samples of the "Alclad" 51SW, which denotes the aluminum-magnesium-silicon alloy, as quenched, have also been welded. Fig. 12 is interesting as showing how the pure metal surface is clearly defined even after welding. Fig. 13 shows the effect of denting the surface of an "Alclad" sheet with a cold chisel. Considerable deformation has been given to the core without entirely cutting through the pure metal.

The author desires to thank Messrs. F. Keller, J. A. Nock, and G. W. Wilcox for preparing the micrographs used in this paper and Messrs. Nock, Keller, T. W. Bossert, and H. H. Richardson, for their part in the development of the product.

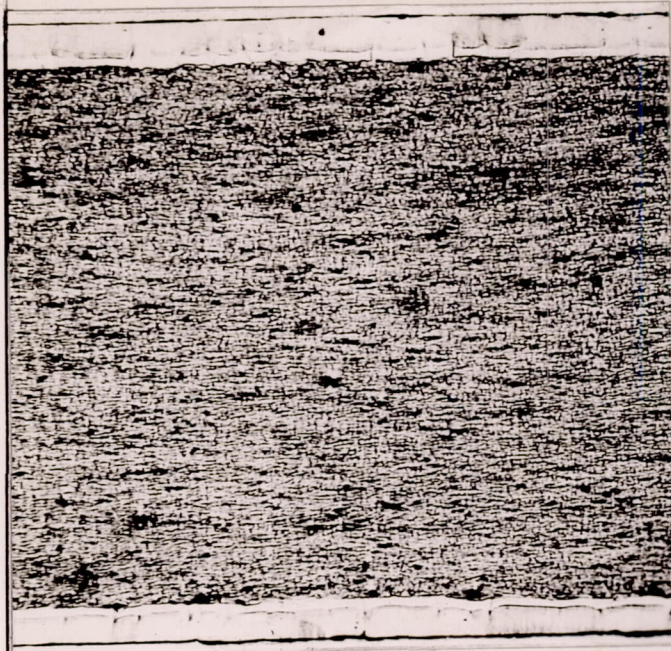


Fig.1 Full cross section of 14 gauge "Alclad" 17ST sheet. Mag. 50X Etched 1 % HF.



Fig.2 Same as figure 1 except magnification. Mag. 100X.

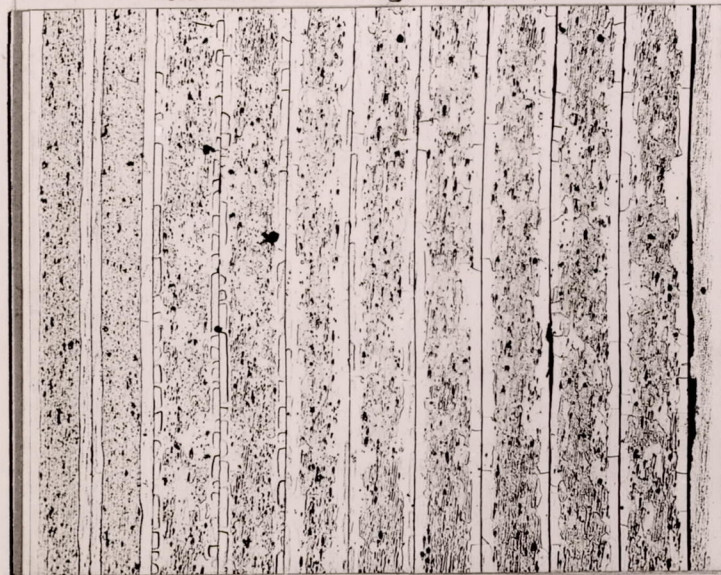


Fig.3 Cross section of composite specimen of ten pieces of "Alclad" 17ST foil 0.003" thick, showing effect of time at heat treating temperature on diffusion of soluble constituents into the pure metal.

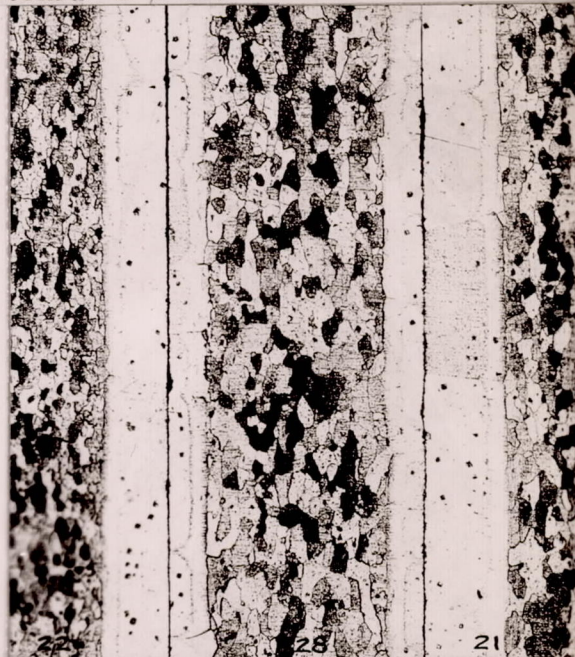


Fig.5 One piece of 28 gauge sheet between pieces of 21 and 22 gauge sheet, water quenched after 10 minutes in nitrate bath at 510°C. Mag. 100X, Etched HF-HCl.



Fig.4 Two pieces of 34 gauge sheet and one piece of 28 gauge sheet, water quenched after 10 minutes in nitrate bath at 510°C. Mag.100X, Etched HF-HCl. 7557 A.S.

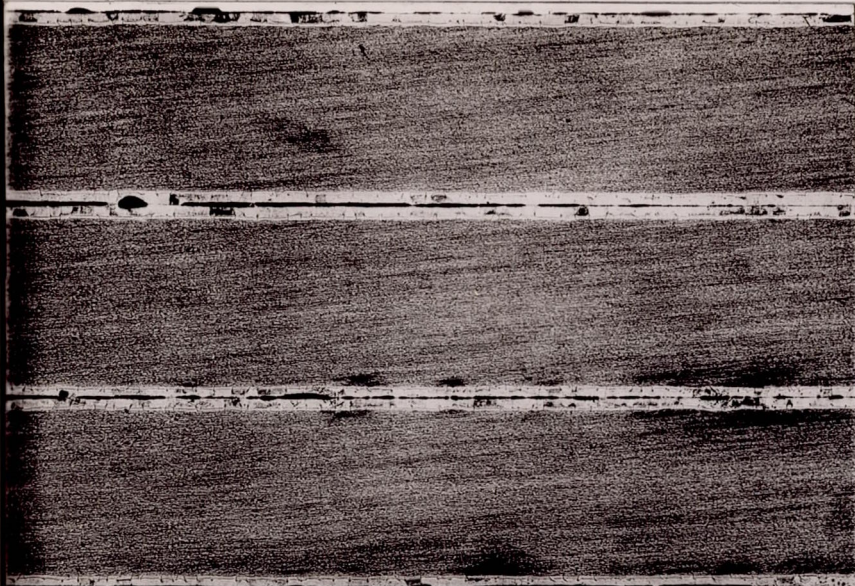


Fig.6 Full cross section of three pieces of 14 gauge "Alclad" 17ST sheet. Mag. 15X, Etched 1% HF.



Fig.7 Full cross section of three pieces of 17SH foil 0.0017" thick rolled from the sheet shown in Fig.6 before heat treatment. Mag.500X, Etched 1/2% HF.

Fig. 8 Illustrates the attack along the machined edge of a tension specimen of 14 gauge normal 17ST sheet after 8 weeks exposure to the salt spray. Mag. 100X, Etched 1/2 % HF.



Fig.9 Illustrates a similar edge of 14 gauge "Alclad" 17ST sheet exposed during the same period as the normal 17ST. Mag.100X, Etched 1/2% HF.





Fig.10 Shows intergranular attack along the edge of 7/16" 20 guage 17ST channel after 48 hours alternate immersion in salt-hydrogen peroxide solution. Mag. 100X, Etched 1/2 % HF.

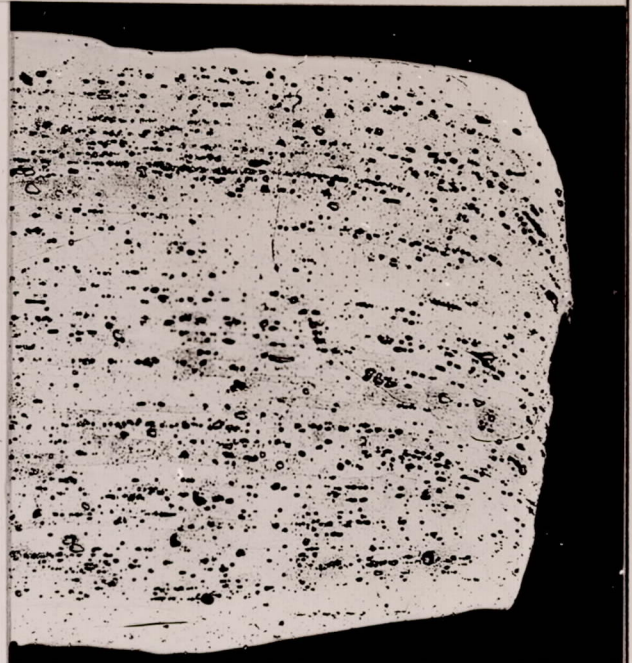


Fig.11 Shows similar edge of the same size channel of "Alclad" 17ST exposed during the same period. Mag. 100X, Etched 1/2 % HF.



Fig. 12

Welded area of a piece of 18 guage (0.040") "Alclad" 51SW Sheet.

Mag. 25X, Etched 1/2% HF.

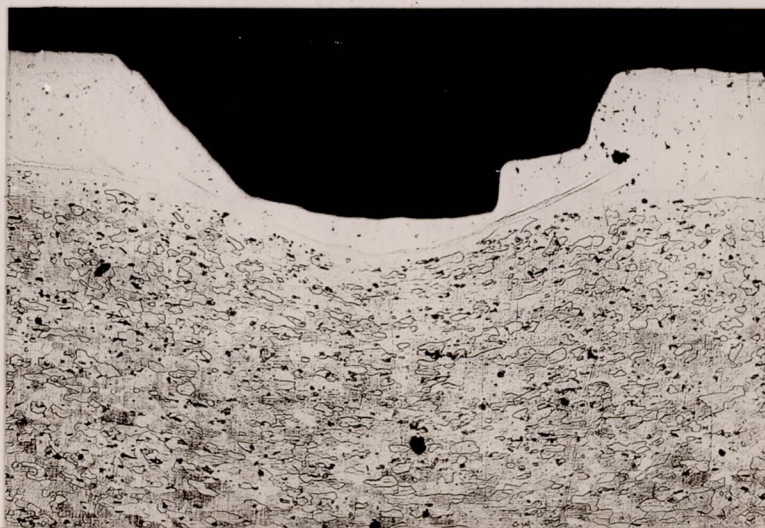


Fig. 13

The effect of an indentation made with a cold chisel in "Alclad" special 17SW 14 guage (0.064") sheet. Mag. 100X, Etched 1/2% HF.