

HETEROGENEOUS ISOTOPIC EXCHANGE AT THE INTERFACE OF STEEL SHEETS IN CONTACT WITH IRON CHLORIDE SOLUTION I.

QUALIFICATION AND PREPARATION OF THE METAL SURFACE

By

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Introduction

The purpose of the investigation into heterogeneous isotopic exchange processes, and within this scope, into exchange processes on metal surfaces (in contact with a solution containing the tracer ions of the metal) is to study both kinetics and mechanism of the exchange processes, and reactivity, structure, self-diffusion etc., by applying these processes (as a method). It can be hoped that the investigation into isotope exchange processes on metal surfaces will result in a method suitable also for investigating the kinetics of heterogeneous reactions on metal surfaces, with special regard to the catalytic action and the corrosion behaviour of metal surfaces. (For this very reason, it is no wonder that in our days the exchange between metals and their ions is the most extensively studied field of the isotopic exchange processes.)

PANETH [1] and HEVESY [2] can be considered as the pioneers of these investigations. A survey of relevant investigations published in the literature is given by HAISSINSKY [7] and WAHL [12]. It is very difficult to compare the results of the various authors, because often the experimental parameters are not known, or the role of some factors (thus e.g. that of the quality of the metal surface) is not properly evaluated.

Literature states a relatively great number of atomic layers of the surface to participate in the isotope exchange on metal surfaces, although in fact, the self-diffusion of metals is negligible at the given temperatures. This is shown by the investigations of HEVESY [2, 3], ROLLIN [4] and COFFIN and TINGLEY [5], who have studied exchange processes between Pb, Ag, Bi, Cu, Sb, Mn, Te, La and their ions at different concentrations, temperatures and pH values, for various durations. L. IMRE and co-workers [6] have been carrying out investigations on the aqueous solutions of carrier-free radioactive metal ions.

Our own investigations concern isotope exchange on the surface of commercial carbon steel. The object of our investigations is the elucidation of the

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theoretical and practical problems of metal corrosion by the study of isotope exchange.

Essentials of the investigated metal surface

In all the experiments in which the physical and chemical properties of the surface of a substance are to be studied, a contaminant free surface must be studied, a contaminant free surface must be prepared, and maintained in this state throughout the experiments.

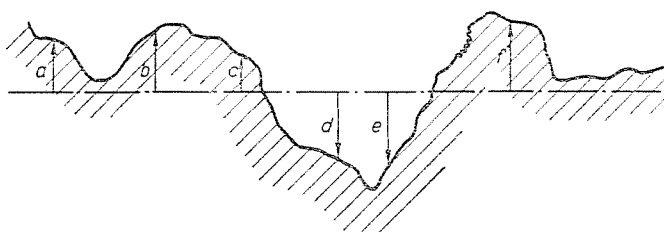
According to an earlier definition, the clean surface is an atomically clean one, which contains only a few percent of monolayer foreign atoms that may either be adsorbed, or substitute the surface atoms of the original lattice.

Practically, metal surfaces may be contaminated by foreign, primarily organic substances (various fats, oils etc.) of extraneous origin or by oxide layers of various thickness, due to atmospheric oxidative agents (oxygen, steam etc.).

ROBERTS [8] describes several methods for the preparation of a clean metal surface, particularly methods using high vacuum. A clean surface according to the above definition can be prepared and maintained at a vacuum of the order of 10^{-9} torr. The cleanness of the surface can be checked by the surface properties of the substance. Many approximations were used with various success. (The surface phenomenon tested can be electron emission, the ionization of gases, e.g. of helium (GOOD and MILLER, 1956), the scattering of low energy electrons (DAVISSON and GERMER, 1927), emission of photoelectrons (EISINGER 1958), secondary electron yield (WANDERSLICE and WHETTEN, 1963), Auger electron emission (MAGSTRUM, 1954) and catalytic reactivity (ROBERTS, 1962). The clean surface can be prepared either by vapour treatment of a split glass or mono crystal surface (in this case, the actual surface can be multiple of the geometrical surface, if the layer is porous), by the chemical ignition of a wire or strip in depression (e.g. an oxidized iron surface can be reduced in hydrogen by ignition for two hours at 850 °C), or by crystal splitting or breaking in vacuum. The application of any of these methods is equipment exacting, and yields in many cases complicated surfaces, which are different from those met in practice, and in our case, unsuitable for the study of isotopic exchange on the surface. Almost without exception, these methods change the original structure of the metal surface, and result in a metal structure other than usual in practice (e.g. a spongy structure). It is principally due to this latter reason that we did not use metal surfaces prepared in the above ways for our investigations. Besides of the high purity requirements emphasis was layed on the intactness of the structure of metal surfaces, as used in practice.

Besides the purity of the surface, the problem of the surface roughness the key issue in the subsequent evaluation of the test results, has been raised.

Theoretically, for determining the surface area, a mathematical plane fitted to the ideal plane of some ideal crystal at absolute zero degree of temperature is considered as the reference surface. In this case atomic stumps, imagined as spheres of the order of 1 Å, give the "unevenness" of the surface, the determination of which — even at room temperature, involving amplitudes of thermal motion — is theoretically possible with the aid of complicated space functions. In practice, the geometrically confined part of the surface (the so-called geometrical surface) is considered usually as the reference surface. The surface can be characterized by the roughness factor, i.e. ratio of the actual to the



$$Ra = \sqrt{\frac{a^2 + b^2 + c^2 + d^2 + \dots}{n}} \quad (\mu m)$$

Fig. 1. The cross section of metal surfaces and the concept of average roughness, characteristic to the surface

geometrical surface. According to ROBERTS [8], the roughness coefficient of e.g. an aluminium layer of 200 Å thickness, vaporized on a glass plate, is 2.5, while that of a radium layer of 200 Å thickness 9. IMRE [6] did not determine the surface of the silver plate used for the isotope exchange investigations, but used in his calculations a roughness factor of 1.5, "estimated on the basis of general experience".

In Hungarian practice, the "surface" of metal objects has been characterized by the "mean roughness (Ra)" of the cross section of the surface (profile), (Fig. 1) given in μm (10^{-3} mm), (Hungarian Standard MSZ 4721—58.)

(For sake of illustration let us mention that permissible surface roughnesses of machine parts are as follows: pistons 1.0 μm , crank arms 0.6 μm , roller bearing slats 6.0 μm . File finishing can produce a surface of 0.4—10 finest grinding 0.16—0.6, and most careful lapping 0.04—0.1 μm roughness.)

The average roughness gives the macroscopic roughness of the surface, which can be measured by various "scanning needle" instruments. Even the grooves producing the macroscopic roughness are not of "geometrical smoothness". Their surface confined by crystal faces broken during processing, gives the microscopic roughness, ranging from 0.03 μm — the linear dimension of a micro-crystal — to the lower limit of macroscopic roughness.

According to the aforesaid, the mean roughness (Ra) describes the grooving of the surface, while the roughness factor is indicative of the increase in

surface area, produced by the roughness. Obviously, these to values are strictly correlated.

Table 1
Increase in surface and roughness factor
calculated for surfaces of various roughnesses according to Fig. 2

Plate No.	Number of peaks on 10 μm of base edge	Pitch height (μm)	Increase of the base edge through peaks in the macro region	Increase through peaks in the micro region (macro + micro base edge (μm) edge of micro-peak: 0.03 μm)	Surface area (μm^2)	Roughness factor
1	1	6	15.6	23.4	550	5.5
2	2	6	26	39.0	1520	15.2
3	1	4	25.6	38.4	1475	14.8
4	2	4	18.8	28.2	795	8.0
5	4	4	33.6	50.5	2550	25.5
6	1	2	10.8	16.2	260	2.6
7	2	2	12.8	19.2	370	3.7
8	4	2	19.2	28.8	830	8.3
9	1	1	10.2	15.3	235	2.4
10	2	1	10.8	16.2	263	2.6
11	4	1	12.8	19.2	368	3.7
12	2	0.5	10.0	15.0	225	2.3
13	5	0.5	11.0	16.5	270	2.7
14	2	0.1	10.0	15.0	225	2.3
15	5	0.1	10.2	15.3	235	2.4

On the basis of theoretical considerations, calculations for a model simulating surface roughness gave for various combinations roughness factors between 2.3 and 25.5 (Fig. 2 and Table 1). With a reference surface of 0.03 μm mean roughness (R_a) (microscopic roughness, i.e. the linear dimension of microcrystals), taking the increase in surface area proportional to the actual mean roughness (R_a) (Table 2). For a surface of a mean roughness of eg. $R_a = 1 \mu\text{m}$ a roughness factor of $x = 33$ will result. (This increase in surface area is illustrated by the profilograms, Figs. 3 through 7.)

The surface of the tested steel sheets was ground with emery paper or grinding wheel of various finenesses. This operation aimed either at removing the surface oxide layer or to "adjust" the surface roughness. The surface roughness of the test sheets has been measured with a GAMMA profilograph, at a needle pressure of 0.1 g. The mean roughnesses of sheets ground with

Table 2

Average roughness values measured with profilograph.
and roughness factors calculated by proportionality

Plate No.	Average roughness measured Ra	Roughness factor calculated
1	0.85	28
	0.73	24
	0.66	22
	0.45	15
3	0.72	24
	0.66	22
	0.71	24
	0.81	27
	0.93	31
	0.98	32
	0.46	15
4	0.45	15
	0.65	22
	0.23	8
	0.30	10
5	0.37	12
	0.75	25
	0.35	12
	0.45	15
6	0.37	12
	0.62	20
	0.58	19
	0.43	14
7	0.50	17
	0.50	17
	0.42	14
9	0.25	8
	0.30	10
	0.27	9
	0.41	14
10	2.2	73
	3.3	110
	3.2	107

Plate No.	Average roughness measured Ra	Roughness factor calculated
13	3.5	117
	4.0	133
	2.3	77
	2.2	73
	2.5	83
15	0.61	20
	0.67	22
16	0.61	20
	0.48	16
20	0.37	12
	0.38	13
	0.33	11
	0.13	4
23	1.9	63

emery paper 320 and 400 (grain size: 0.063—0.050 and 0.040—0.028 mm ranged between 0.13 and 0.85 μm respectively, Table 2), while the Ra values of sheets ground with a grinding wheel were 1.9 to 4.0 μm . Roughness factors were calculated by proportionality from Ra values measured (Table 2) for the evaluation. Since the profilograph recorded Ra values differing by as much as 50 per cent even on identical surfaces, considered as homogeneous, in the evaluation of the results a relevant error of 50 per cent must be reckoned with, leaving other methods applied in our tests without consideration.

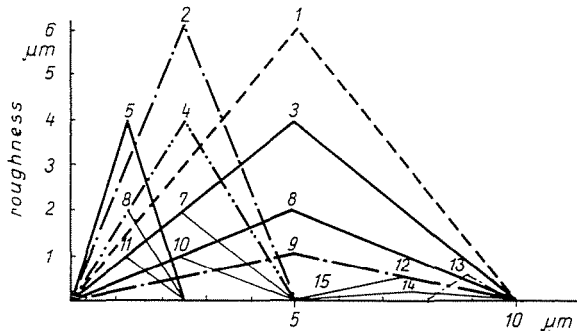


Fig. 2. Symbolization of the surface roughness for different variants, in accordance with numerical values in Table 1

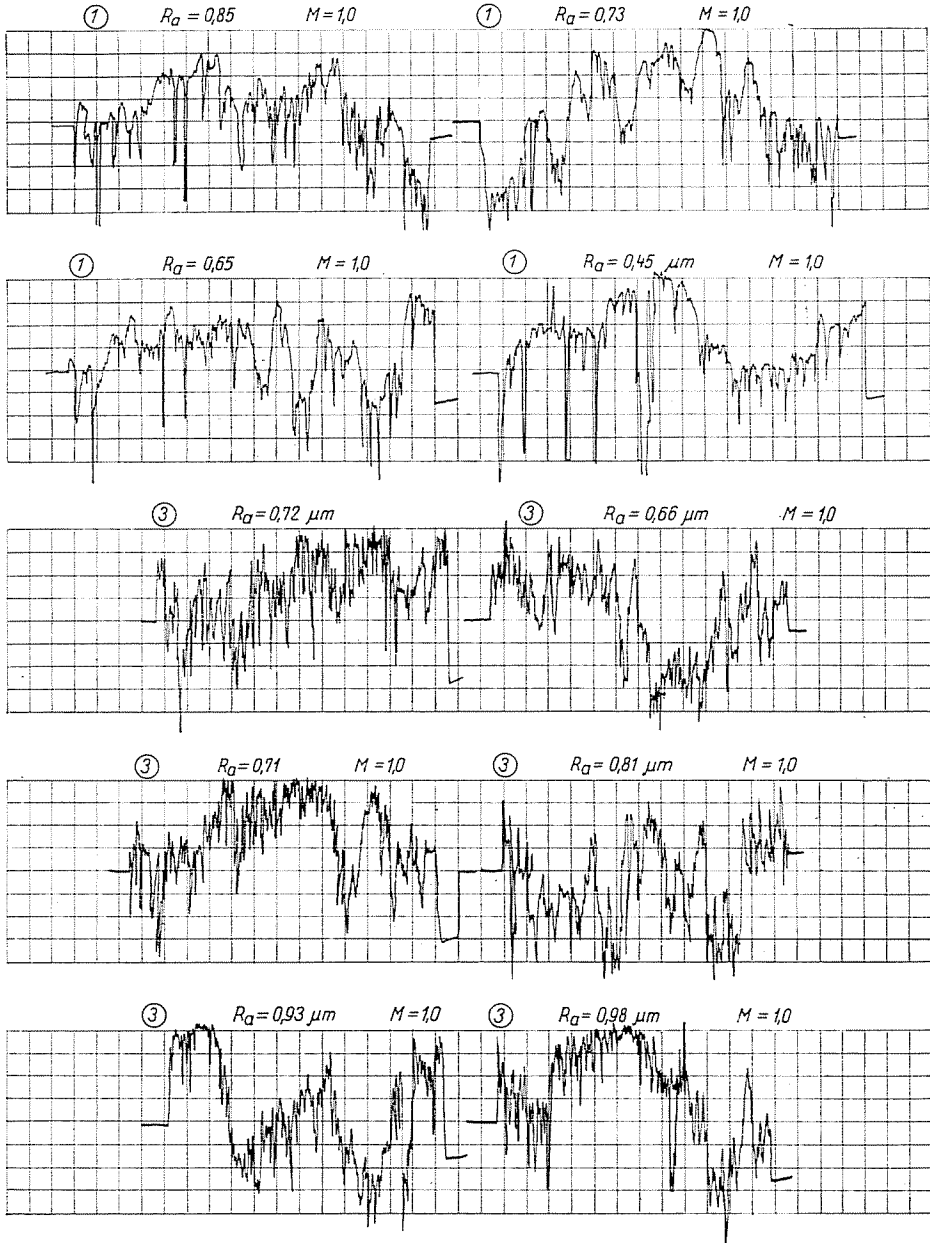


Fig. 3. Profilograms of ground (polished) surfaces

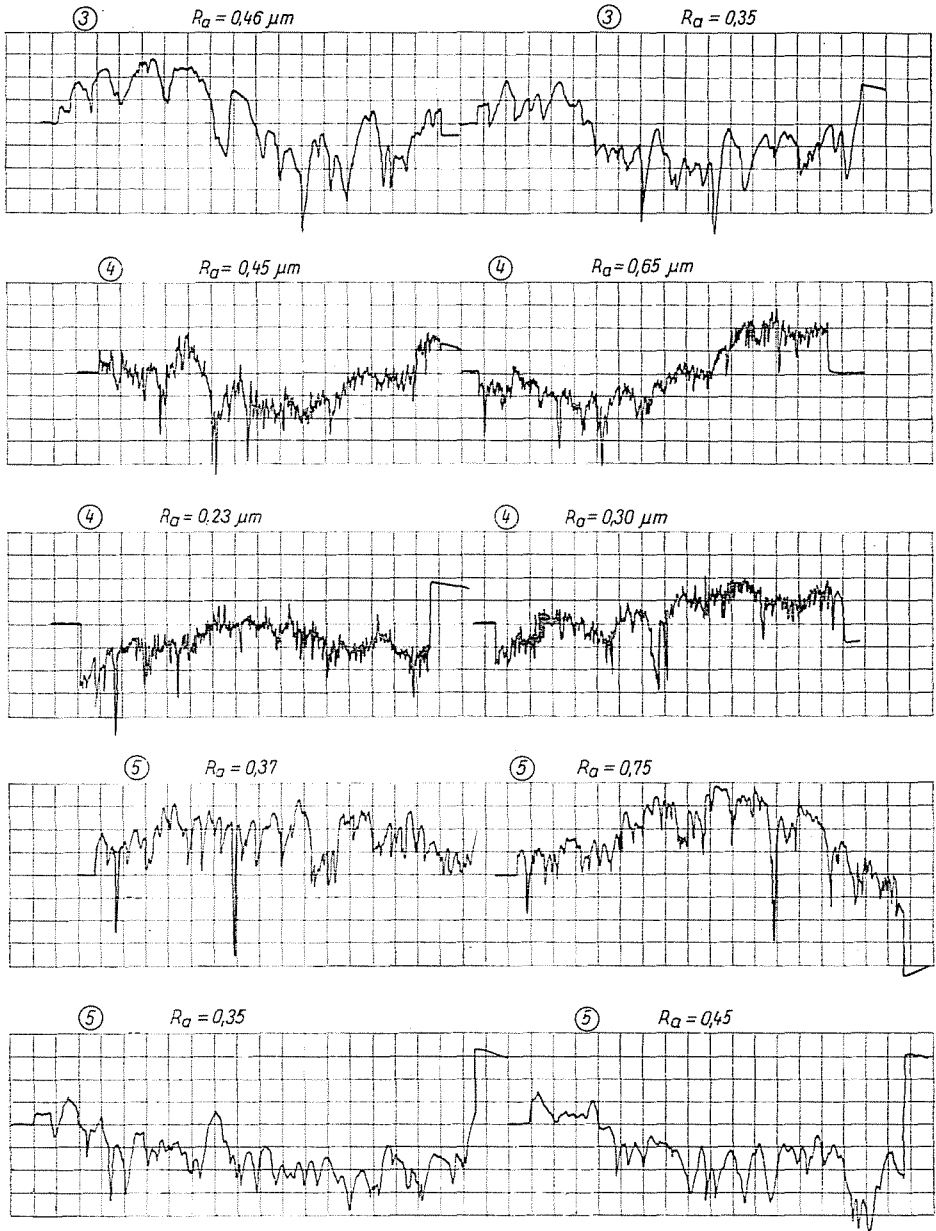


Fig. 4. Profilograms of ground (polished) surfaces

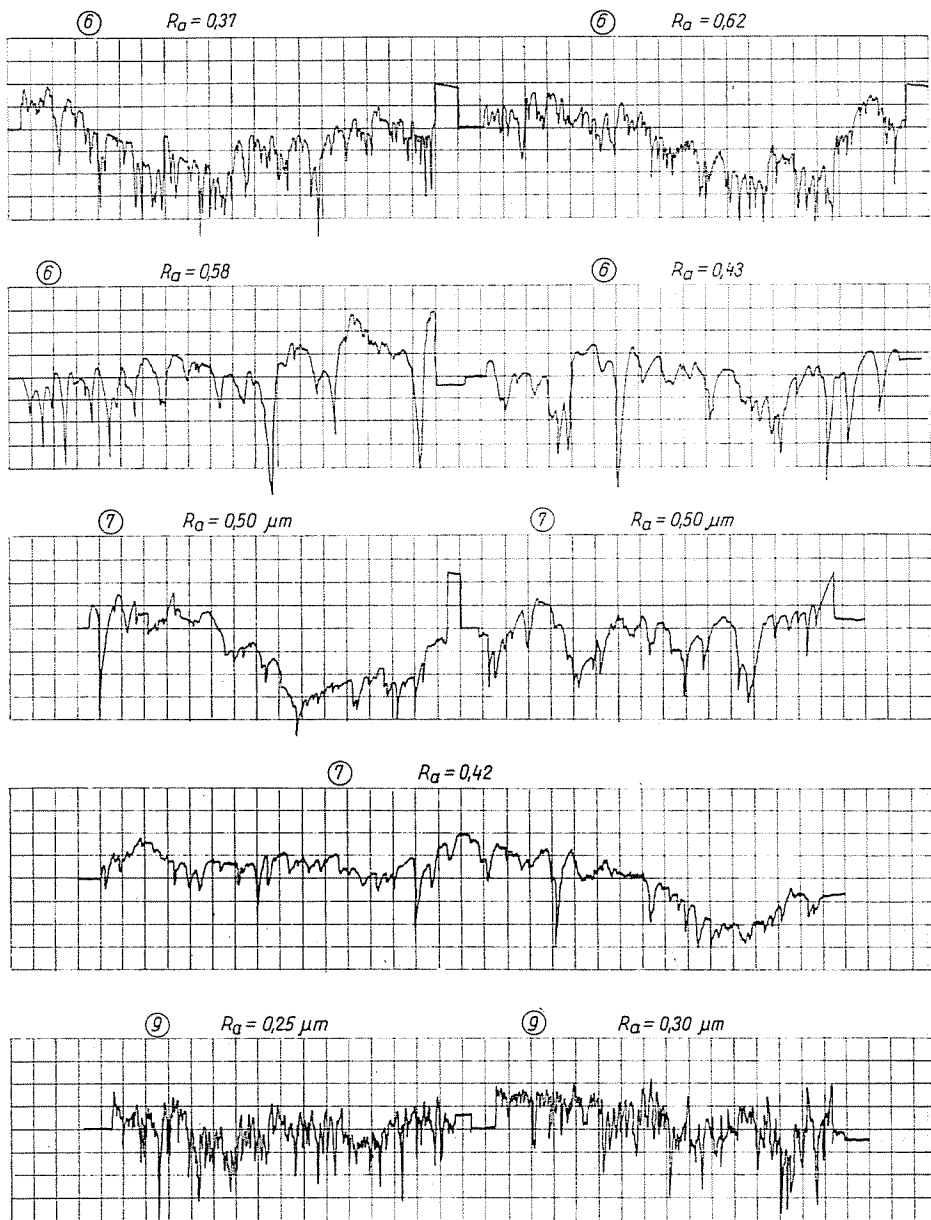


Fig. 5. Profilograms of ground (polished) surfaces

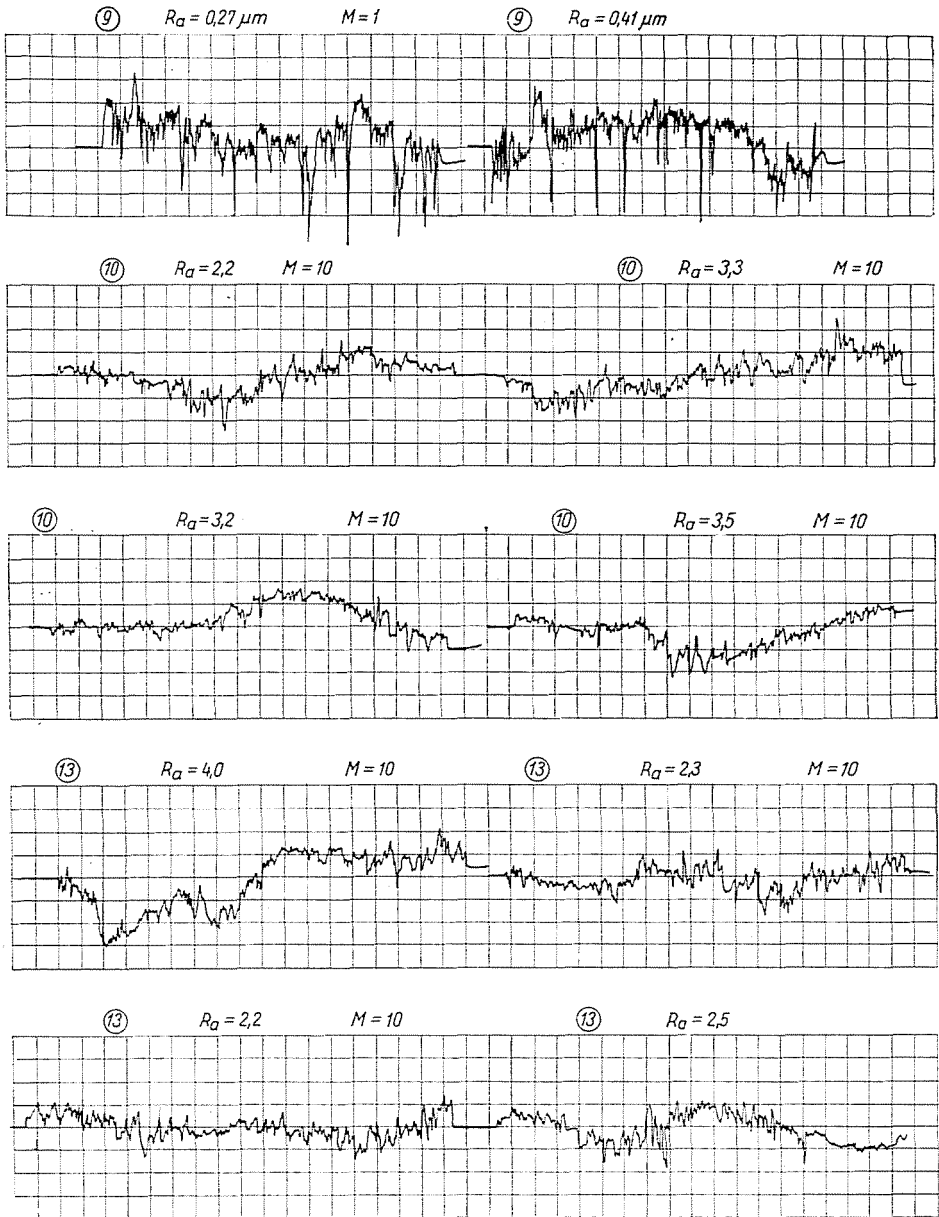


Fig. 6. Profilograms of ground (polished) surfaces

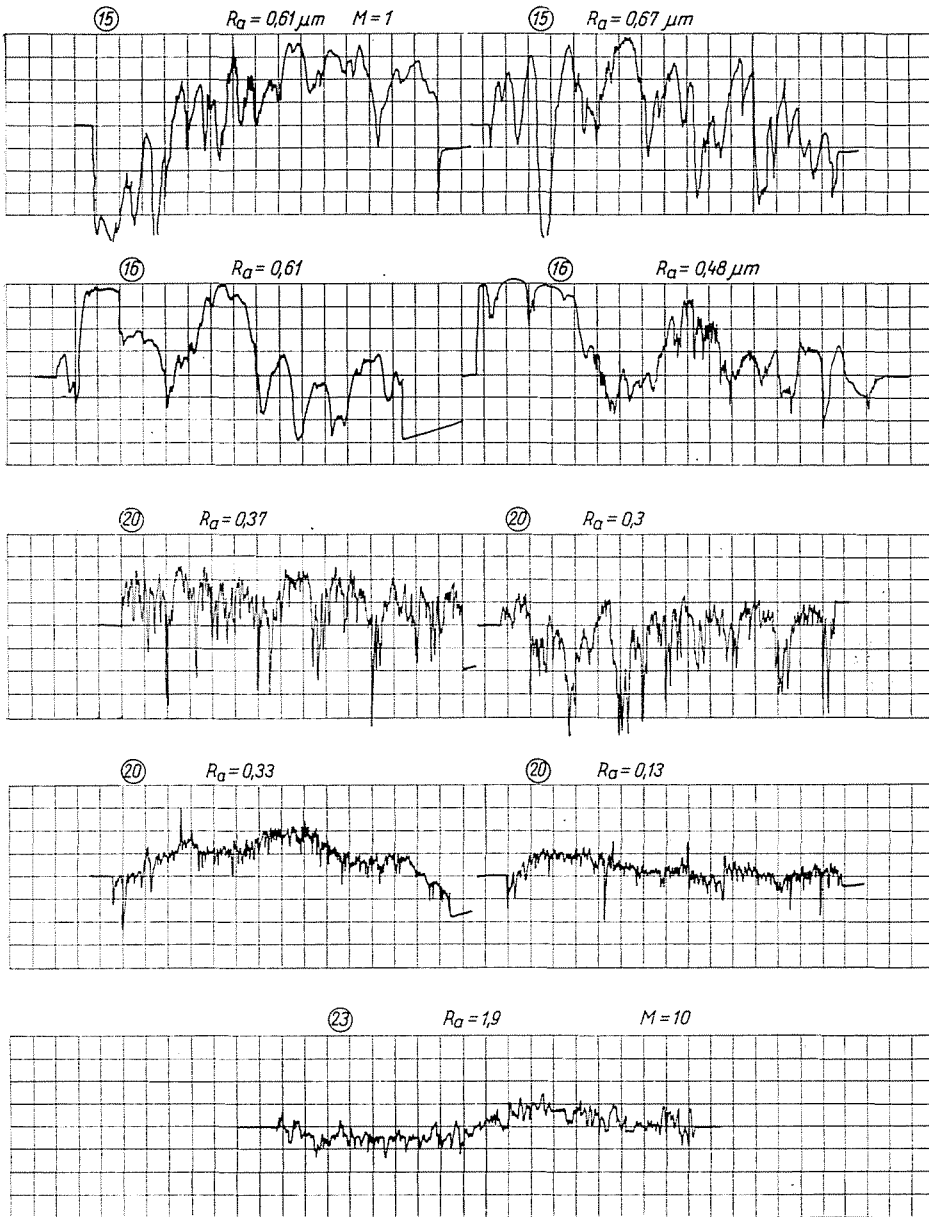


Fig. 7. Profilograms of ground (polished) surfaces

For when investigating metal surface phenomena, the surface roughness is seen to be of a great importance for the evaluation of the results. There is no reliable measuring method, however, for such relatively small surfaces.

Tested sheet surfaces were cleaned after grinding from eventual fatty substances and residual emery grains in an alkaline solution, by electrolytic defatting. The test specimens were connected as cathode, so that the disengaged hydrogen should remove the oxide layer that might form during grinding. According to our earlier investigations, a steel surface purified in this way would contain not more than 10^{-7} g/cm² of residual impurity [9], hence the surface might be considered practically clean [10]. The plates were subsequently rinsed, and tested without contacting air.

Chemical composition of the metal surfaces

As concerns chemical composition there is a great variety of commercial steels. Contaminants and alloying elements considerably influence the chemical and physical behaviour of steels.

Similar investigations reported of in the literature, have mostly been made on polycrystalline (e.g. Cu, Ag) (seldom on monocrystalline) pure metals ones. A novel feature of our investigations was to test a commercial cold rolled steel. The chemical composition of the steel plates is shown in Table 3.

Table 3

The chemical composition of the tested cold rolled steel plates

	C	Si	Mn	S	P
Plate I (0.75 mm)	0.035	0.04	0.39	0.015	0.014
Plate II (1.2 mm)	0.029	0.03	0.36	0.020	0.017

Cu	Cr	Ni	Mo	V	W	Al	Ti
0.10	<0.10	<0.10	<0.05	0.05	—		0.01
0.19	<0.10	<0.10	0.09	ny	—		ny

Summary

A definition is given of the surface of steel plates used for the investigation into heterogeneous isotope exchange processes. Surface purity and the increase in surface area due to surface roughness have been determined. Methods for preparing the surface and control tests of the surface have been presented.

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