A computer-controlled time-of-flight atom-probe field-ion microscope for the study of defects in metals

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Abstract A time-of-flight (TOF) atom-probe field-ion microscope (FIM) specifically designed for the study of defects in metals is described. This atom probe features (i) a variable-magnification internal image-intensification system based on a channel electron multiplier array for viewing the FIM image; (ii) a liquid-helium-cooled goniometer stage which allows the specimen to be maintained at a temperature anywhere in the range 13-450 K; (iii) a low-energy (<3 keV) gas ion gun for in situ irradiations; (iv) a ultra-high-vacuum (about 4 x 10^{-8} Pa) chamber to minimize specimen contamination; (v) a high-vacuum (about 1.3 x 10^{-4} Pa) specimen-exchange device; (vi) a Chevron ion detector; and (vii) an eight-channel digital timer with ±10 ns resolution for measuring the TOF of the field-evaporated ions.

The entire process of applying the evaporation pulse to the specimen, measuring the DC and pulse voltages and analysing the TOF data is controlled by a Nova 1220 computer. Data in the form of a histogram of the number of events plotted against the mass-to-charge ratio are displayed on a Tektronix graphics terminal. An extensive set of computer programs to test and operate the atom-probe FIM has also been developed. With this automated system we can record and analyse 600 TOF min^{-1}. The instrument can clearly resolve the seven isotopes of molybdenum and the five isotopes of tungsten. Investigations of alloys have shown that the concentration of rhenium in a W-25 at. % Re alloy, and the concentrations of titanium and zirconium in Mo-1 at. % Ti and Mo-1 at. % Ti-0.08 at. % Zr alloys can be easily measured. Investigations of a low-swelling stainless steel alloy (LS1A) and a metallic glass alloy (Metglass 2826) have shown that all constituents present at a level of 0.05 at. % or higher can be readily determined.

1 Introduction
The time-of-flight (TOF) atom-probe field-ion microscope (FIM) (hereinafter to be referred to as an atom probe) is basically a FIM combined with a special TOF mass spectrometer (Müller et al 1968). Figure 1 illustrates the main features of the atom probe. A specimen with a radius of approximately 50-500 nm is maintained at a positive potential of about 5-20 kV so that gas atoms surrounding the specimen are ionized over individual atomic sites and are projected radially outward to produce an image of the atoms on the internal image-intensification system. When a short high-voltage pulse is applied, atoms on the surface of the specimen are field-evaporated in the form of ions. Those ions projected into the probe hole at the centre of the intensification system will pass down the flight tube to the Chevron ion detector. The TOF of the ions and the voltage on the specimen are measured and used to determine the mass-to-charge ratios m/n of the field-evaporated ions. The operation of the atom probe is controlled on-line by a Nova 1220 minicomputer which triggers the high-voltage pulse to the tip, reads in the TOF and voltage data and then calculates the m/n values of the ions. The computer operates in real time so that results are available immediately on the graphics display terminal for interpretation as the experiment progresses.

Since the first publication concerning an atom probe by Müller et al (1968), a number of other instruments have also been reported in the literature and also described at field emission symposia (Brenner and McKinney 1968, 1970, Turner et al 1973, Kinosita et al 1974, Wagner et al 1975, Gallott et al 1975, Lewis and Smith 1975, Watts and Ralph 1975, Chambers and Ehrlich 1975, Andren and Norden 1975, Krautz et al 1976). The major metallurgical applications of the atom probe to date are (a) a study of the early stages of precipitation in Fe(Cu) alloys by Goodman et al (1973a, b) and in the Fe-3 at. % Mo system (Brenner and Goodman 1971); (b) an analysis of precipitates in iron and steels by Turner and Papazian (1973); and (c) an investigation of chromium depletion near the surface of a 410 stainless steel by Krishnaswamy et al (1974). In addition, Müller and Tsong (1973) and Panitz (1975) have written review articles on single-atom mass spectrometry to which the reader is referred for details on the physics of the atom probe.

The atom probe is ideally suited for the study of the interactions of lattice defects with impurity atoms and alloying elements in metals. The basic reason for this is that by controlled, pulsed-field evaporation of successive atomic layers it is possible to examine the bulk of the specimen and reconstruct in three dimensions the correspondence between specific microstructural features and chemical composition. More specifically the atom probe is capable of imaging lattice defects such as vacancies, self-interstitials atoms (SIA), dislocations, grain boundaries and voids, and can also chemically identify both substitutional and interstitial alloying elements or impurity atoms.

In §§2-4 of this paper we describe an ultrahigh-vacuum (UHV), computer-controlled atom probe with a number of unique features that make it ideally suited for studying metallurgical problems, particularly defects in metals. Many details concerning the actual construction of this instrument are contained in an unpublished report (Hall et al 1975) which has been summarized in a short paper (Hall et al 1976). Section 5 of this article contains the results of a number of atom-probe experiments which demonstrate the instrument's ability to examine a wide variety of pure metals, metal alloys and metallic glasses.

2 Field-ion microscope system
2.1 Internal image-intensification system and focusing lens
As shown in figure 1 the FIM image is observed with the aid of an internal image-intensification system consisting of a Galileo 75 mm diameter channel electron multiplier array (CEMA) and a

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phosphor screen (Rosebury 1965). The CEMA has a particle
the FIM specimen, the internal image-intensification system,
looking lens, the 45° viewing mirror, the Chevron ion
detector and the low-energy gas ion gun for performing
in situ irradiations. The digital timer and specimen voltage

Figure 1 The top atom-probe FIM. Shown at the top of the
figure are the internal elements of the atom probe including the
FIM specimen, the internal image-intensification system,
the focusing lens, the 45° viewing mirror, the Chevron ion
detector and the low-energy gas ion gun for performing
in situ irradiations. The digital timer and specimen voltage

phosphor screen (Rosebury 1965). The CEMA has a particle
gain of more than $10^3$ which makes direct observation of the
FIM image easy even at an imaging gas pressure as low as
1.33 x $10^{-4}$ Pa (Turner et al 1969, Brenner and McKinney
1970). The beam of pulsed-field-evaporated ions passing
through the 3 mm hole in the intensification system is shielded
from the potentials on the CEMA and screen by a stainless steel
tube with a 25 $\mu$m thick wall at ground potential. This tube is
electrically insulated from the CEMA and screen by a glass tube
with a 50 $\mu$m thick wall. To further shield the ion beam, the
back side of the glass screen was given a separate coating of tin
oxide which is maintained at ground potential.

Immediately behind the image-intensification system (see
figure 1) is a focusing lens in the form of a stainless steel bushing
which passes through a glass plate coated on both sides with
tin oxide. This lens is maintained at a voltage proportional
to the DC voltage on the specimen (see §3.1). Behind the focusing
lens is a front-surfaced glass mirror, placed at 45° to the
flight path, which contains a 10 mm diameter hole through its
centre. The hole is lined with a grounded, stainless steel sleeve
which prevents charged particles from accumulating on the
exposed glass surfaces. The FIM image is photographed with an
Autocam 35 mm cine camera.

The entire assembly consisting of the internal image-intensi-
fication system, focusing lens and viewing mirror is attached to
two UHV metal bellows (Metal Bellows Co., Sharon, Mass.)
arranged so that the distance from the specimen tip to the front
surface of the intensification system is continuously variable.
By this means the tip-to-image intensification system distance
can be varied from about 12 mm to 100 mm, thus providing a
linear magnification change of $\geq 8 \times$ and an area magnifica-
tion change of $\geq 64 \times$.

2.2. Helium-cooled goniometer stage
A liquid-helium-cooled goniometer stage has been constructed
with the following features: (i) the specimen can be quickly
cooled to cryogenic temperatures to improve the quality and
resolution of the FIM image and also to change the diffusivity of
point defects such as SIA; (ii) the specimen can be rotated by
$\pm 70°$ about two orthogonal axes which intersect at the tip of
the specimen, so that a selected region of the specimen can be
projected over the probe hole for chemical analysis; and (iii)
the goniometer stage can be translated in three mutually
orthogonal directions ($x, y, z$) to facilitate the alignment of the
tip with respect to both the probe hole and the low-energy gas
ion gun described in §2.3.

A cut-away view of the helium-cooled goniometer stage is shown in figure 2. The FIM specimen is mounted in a copper
specimen holder which is removed when one specimen is
exchanged for another. This holder is threaded into a copper
plate bolted on to the back of the upper sapphire electrical
insulator. On the top of the insulator is a copper plate into
which are clamped 50 strands of 0.3 mm diameter high-purity
gold wire. The upper end of this inner cooling braid is clamped
to the lower end of the cryostat. The liquid helium cryostat is
similar to the one described previously by Seidman et al (1969),
but the design has been modified to take increased advantage
of the cooling power of the cold helium gas produced by the
liquid helium that boils off during the initial cool-down period.

The conduction heat load on the specimen holder was
minimized by supporting the sapphire block containing the
specimen holder on a stainless steel tube with a 50 $\mu$m thick
wall. The radiation heat load was minimized by surrounding
the specimen holder with a copper radiation shield that is
cooled to within 50 K of the tip temperature by the helium
exhaust gas escaping from the cryostat. Because of these
features the total heat load on the specimen holder is small
(abut 0.3 W) compared to the total cooling capacity of the
gold braid (about 5 W). Tests of the cryostat's performance

† All pressures reported in this text are gauge pressures.
Figure 2. Diagram of the goniometer stage which allows the FIM specimen to be rotated about two mutually orthogonal axes. The liquid helium cryostat is connected to the specimen mount via a flexible gold braid. The copper radiation shield surrounding the specimen mount is cooled by a second gold braid which is also connected to the cryostat.

showed that the FIM specimen is cooled to 30 K within about 20 min and to 13 K within 1 h with a liquid helium consumption rate of approximately 1.5 l h⁻¹ at 13 K. At temperatures greater than about 30 K the consumption rate drops to roughly 0.1 l h⁻¹. In routine operation the temperature is measured with a platinum resistance thermometer (PRT) located on the tail of the cryostat (see figure 2). The specimen temperature has been calibrated with respect to this PRT.

The goniometer supporting the cryostat was adapted from plans supplied by Dr S S Brenner of the US Steel Corporation. This goniometer provides the rotation about two orthogonal axes while maintaining UHV conditions by the use of two linear-motion, stainless steel UHV bellows seals. The lateral position of the tip varies by less than 1 mm when the tip is rotated through its full arc, due primarily to the compact design of the goniometer stage. The portion of the goniometer external to the FIM is mounted on three machinist's slides and is connected to the vacuum system through a bellows seal so that it can be translated in three mutually orthogonal directions to facilitate alignment of the tip with respect to the flight tube and the ion gun.

2.3 Low-energy gas ion gun

A simple, low-energy gas ion gun (Hall et al 1975) has been constructed to enable us to irradiate FIM specimens in situ as shown in figure 1. In operating the ion gun a gas such as H₂, He, Ne, Ar or Xe is continuously bled through a stainless steel cylindrical plasma chamber held at a positive potential. The gas is ionized in the chamber by a magnetically confined 2 mA beam of 30–100 eV electrons emitted from a heated tungsten filament. The ions produced in the plasma chamber are extracted, accelerated and focused on to the FIM specimen. The vacancies may then be completely removed by field-evaporating away several surface layers. This is the only presently known mechanism of producing a point defect state consisting solely of isolated SIAS. The ion gun is also used to implant gas atoms, such as hydrogen, in the tip of the FIM specimen.

An experiment testing the performance of the low-energy gas ion gun was conducted in which a tungsten specimen maintained at 30 K was irradiated with 275 eV Ne⁺ ions. After the removal of the damaged surface layer by field evaporation an isochronal-annealing experiment was performed which revealed the presence of SIAS migrating to the surface of the FIM tip as expected (Scanlan et al 1971a, b, Seidman 1973, Wilson and Seidman 1975, Seidman et al 1975, 1976).

2.4 Ultrahigh-vacuum system

The use of a UHV system minimizes the interaction of residual gas atoms with the FIM specimen in two important ways. First, it reduces the probability of the formation of (metal-atom)-(gas-atom) complexes and thereby reduces the number of peaks observed in the m/n spectra. Secondly, it reduces the concentration of artefact contrast effects which are produced as a result of (impurity-gas-atom)-(surface-atom) interaction (e.g. artefact vacancies (Berger et al 1973) and artefact SIAS (Seidman and Lie 1972, Robinson et al 1973)). This second point is important for our research, since we are involved in the study of the interaction of both substitutional and interstitial atoms with point defects.

The primary vacuum pumps are a large titanium sublimation pump (TSP) and a 140 l s⁻¹ ion pump. The vacuum chamber is initially rough-pumped by two sorption pumps used in sequence. The use of the TSP, ion pump and sorption pumps maintains ultra-clean conditions and avoids contamination with pump oil. A 5 cm diameter oil diffusion pump is used to pump the main chamber when the atom-probe FIM contains an imaging gas (e.g. helium or neon) since the TSP and ion pumps cannot be used for this purpose. At all other times the diffusion
pumps are valved off to prevent possible backstreaming of oil into the vacuum system. Ultimate pressures of \(4 \times 10^{-3}\) Pa are obtained after baking to 150°C for several hours, while under typical operating conditions the pressure is \(1.33 \times 10^{-2}\) Pa.

2.5 Specimen-exchange device

A specimen-exchange air lock was incorporated into the design of the atom probe to allow the FIM specimen to be replaced without exposing the vacuum system to atmospheric pressure. For the exchange of a specimen the FIM specimen holder is attached to the end of a 1 m long, 9.5 mm diameter specimen-exchange rod with a bayonet clip. The specimen-exchange rod passes through a Wilson-type sliding motion feedthrough sealed with two Viton O-rings. The air lock is rough-pumped using two sorption pumps in sequence and it is then pumped to \(<1 \times 10^{-4}\) Pa by a triode ion pump. Under typical conditions the pressure in the main chamber remains below \(1.33 \times 10^{-3}\) Pa during the exchange and drops to \(4 \times 10^{-2}\) Pa within 15 min after the exchange port has been closed.

2.6 Residual gas analyzer

A Uthe Technology Inc. (UTI) Model 100C residual gas analyzer was installed on the atom-probe rim, allowing us to determine the composition of the residual gases in the vacuum system. This instrument has proved to be particularly valuable for determining whether specific impurity atoms originated in the specimen or were artefacts of the vacuum conditions. For example, the instrument has been used to determine the CO and CO2 levels in the vacuum system, thus aiding in the interpretation of the peaks observed at atomic mass 16 which could be due to either titanium in a specimen or oxygen from the vacuum system; oxygen can be produced as a result of the decomposition of CO or CO2 on metal surfaces.

3 Time-of-flight mass spectrometer

To determine the \(m/n\) ratios of the pulsed-field-evaporated ions the voltage on the specimen is measured by an analogue-to-digital (A/D) converter and the \(m/n\) ratios of the ions are measured by a digital timer (Berger 1973). The \(m/n\) voltage and data are sent to the computer which calculates the mass-to-charge ratios \(m/n\) from the equation (Pantz et al 1969)

\[
m/n = 2e(V_{DC} + aV_{pulse})(t - t_0)^2/d^2,
\]

where \(e\) is the charge of the electron, \(V_{DC}\) is the steady state imaging voltage, \(V_{pulse}\) is the evaporation pulse voltage, \(a\) is the so called pulse factor, \(d\) is the flight distance and \(t - t_0\) is the actual \(m/n\) of the ion. The quantity \(t\) is the observed \(m/n\) and \(t_0\) is the total delay time. The controls of the \(m/n\) pulse and focusing-lens power supplies are coupled together so that the pulse and lens voltages are always a constant fraction of the \(m/n\) voltage; this technique simplifies the calibration procedure and optimizes the resolution of the atom probe as discussed by Wagner et al (1975).

Typically the pulse voltage is maintained at 0.04-0.20 of \(V_{DC}\) and the lens is maintained at 0.3-0.5 of \(V_{DC}\). Below approximately 0.04 \(V_{DC}\) the pulser behaves erratically and the continuous \(m/n\) field evaporation rate becomes comparable to the pulsed-field evaporation rate. Above 0.20 \(V_{DC}\) the increased spread in the energy of the field-evaporated ions degrades the mass resolution of the spectrometer.

3.1 Specimen voltage system

The voltage on the specimen must be precisely controlled and measured if accurate \(m/n\) values are to be obtained employing equation (1) or (3). The FIM specimen is connected to a CPS 100R, 30 kV power supply through a 10 kΩ blocking resistor. A 20 ns high-voltage evaporation pulse \(V_{pulse}\) with a rise time of \(<0.2\) ns produced by a modified Cayuga Associates CA101 mercury relay pulser is coupled to the specimen through a 30 kV, 47 nF capacitor. A Spellman RHR 10PN100 high-voltage dc power supply is used to provide the voltage to the pulser. The values of \(V_{DC}\) and \(V_{pulse}\) are measured with an Analogic 5800 series, 13-bit, 16-channel A/D converter. The outputs of the high-voltage power supplies are reduced by precision voltage dividers (Hall et al 1975) to bring these voltages within the 10 V maximum range of the A/D converter.

The high-voltage power supplies, the voltage dividers and the A/D converter were tested by monitoring the measured voltage with the aid of the computer and comparing it with the known voltage obtained using a high-precision Hewlett-Packard 3439A digital voltmeter. These tests indicated that the measured voltages are accurate to within 5 V (which corresponds to 1 bit in the A/D converter) and that the voltages are stable to within \(<5\) V over periods of several hours.

3.2 Chevron ion detector

The ion detector at the downstream end of the flight tube consists of two 25 mm diameter CEMAS in the Chevron configuration and a phosphor screen (Colson et al 1973). The 37.5 μm diameter channels in the first CEMA are at 5° to the normal to the front surface of the CEMA to prevent secondary-ion feedback through both CEMAS. Behind the CEMAS is a 25 mm diameter phosphor screen which is capacitively coupled to a LeCroy Research System (LRS) 133B dual amplifier operated at a gain of 25. The output pulse from the amplifier is delayed by 500 ns (by about 150 m of RG 58 cable) and then triggers one channel of an LRS 161 discriminator which stops the digital timer. The Chevron detector was chosen because its particle detection characteristics are good (Brenner and McKinney 1972, Muller et al 1973) and it provides a visible image of the ion beam which is extremely useful for the alignment and focusing of the \(m/n\) mass spectrometer.

If small concentrations of impurity atoms or alloying elements are to be reliably detected the Chevron ion detector must be well characterized with respect to spurious output pulses. Tests of our detector indicate that the random background count rate is approximately 10 s⁻¹ which indicates that impurity atom concentrations in the 10 appm range can be detected. The rate of occurrence of artefact pulses following the true pulse by up to 10 μs is less than 0.2%.

3.3 Digital timer

The digital timer that we have constructed can measure \(m/n\) as long as 99 00 μs of up to eight consecutive field-evaporated ions with an accuracy of 0.01 μs. The basic features of this timer have been described in an earlier paper (Berger 1973). The version presently being used has a number of modifications which were introduced to improve the accuracy and reliability of the timer, the principal modification being that

\[†\] The capability of measuring the \(m/n\) of up to eight ions has proved useful particularly when examining crystallographic regions in which it is difficult to prevent several ions from field-evaporating due to a single evaporation pulse. For example, in examining the (110) plane of W, we have found that two or more W ions were detected in over one-half of the evaporation events even though the average evaporation efficiency was only about 0.01 ion per evaporation pulse.
the start signal from the pulser and the stop signals from the Chevron ion detector are synchronized with the timer's clock so that problems caused by changes of logic state during clock transitions are completely eliminated. To test the digital timer, the resolution of the TOF atom probe has been discussed at the computer. In over 10^6 operations no errors have been detected with the modified timer, indicating that the tofs measured during experiments can be treated with confidence (Hall et al 1975).

3.4 Resolution of the TOF mass spectrometer

The resolution of the TOF atom probe has been discussed at length in the literature (e.g. see Müller and Krishnaswamy 1974, Regan et al 1976). There are three major factors affecting the resolution: (1) inaccurate determination or variations of the calibration parameters, (2) uncertainty in the measurement of the TOF and voltage on the specimen; and (3) energy deficits.

By maintaining \( V_{\text{pulse}} \) at a constant fraction \( f \) of \( V_{\text{DC}} \), so that

\[
V_{\text{pulse}} = fV_{\text{DC}},
\]

equation (1) becomes

\[
m/n = (2e/d_{\text{eff}}^2)\frac{V_{\text{DC}}}{V_{\text{DC}}(1-t_0)^2}
\]

where

\[
d_{\text{eff}} = d/(1 + d/f)^{1/2} = \text{constant}.
\]

This technique reduces the number of calibration parameters to two, namely \( d_{\text{eff}} \) and \( t_0 \), thus eliminating the need for an accurate, independent determination of \( d \). Furthermore, the calibration parameters \( \alpha \) and \( d \) now only affect the absolute values of \( m/n \), so inaccuracies in their determination do not affect the mass resolution \( \Delta m/m \) of the atom probe. The remaining calibration parameter \( t_0 \) can be measured electronically to a high degree of accuracy and poses no problem. In all of our work to date we have never found the basic shape of the spectrum to depend on the exact determination of the calibration parameters. Both \( \alpha \) and \( t_0 \) can be held constant if high-quality, low-drift electronics are employed. Thus the only remaining factors which affect the resolution are the uncertainties in the TOF and voltage measurement, variations in \( d \) and energy deficits.

For our mass spectrometer with a time uncertainty of \( \pm 10 \) ns, a voltage uncertainty of \( \pm 3 \) V and a flight path length variation of \( \pm 0.05 \) mm, a standard calculation of the \( m/n \) uncertainty for \( ^{180}\text{W} \) results in \( \Delta m/m = 62 \alpha \) with a total voltage \( (V_{\text{DC}} + \alpha V_{\text{pulse}}) \) of 15 kV and \( d = 1600 \) mm predicted a full width at half-maximum (FWHM) of \( \leq 0.20 \) u and a full width at 0.1 maximum of \( 0.34 \) u. The measured FWHM for \( ^{180}\text{W} \) (see figure 3(a) in Hall et al 1976) was 0.2 u while the full width at 0.1 maximum was 0.7 u; the first criterion yields a \( \Delta m/m \approx 1/300 \) while the latter criterion yields \( \Delta m/m \approx 1/90 \).

The observed FWHM value is in good agreement with the predicted value while the observed full width at 0.1 maximum is considerably greater than the predicted value. All of the peaks observed to date were sharp on the leading edge with a tail extending to the high-mass side of each peak (e.g. see figure 2 in Hall et al 1976 for the Mo\(^{19}\) spectrum and figures 4, 5 and 6 in this paper). This large tail contributes strongly to the observed full width at 0.1 maximum and only weakly to the FWHM value. The observation of this high-mass tail appears to be quite general for all straight TOF atom probes and has been attributed to energy deficits associated with the field evaporation process (Müller 1971, Krishnaswamy and Müller 1974). In addition, Regan et al (1976) have also analysed the energy deficit problem in terms of pulse shape and the decay behaviour of the evaporation pulse. At present the best approach to eliminate energy deficits, and thereby to increase the \( \Delta m/m \) value to about 1/1000, appears to be through the use of the isochronous focusing lens designed by Poschenrieder (1972) and adapted by Müller and Krishnaswamy (1974) to the atom probe. We emphasize strongly that the straight TOF atom probe has a resolution sufficient for the study of a wide range of materials. For example, the practical resolution of our instrument is clearly about 1/200 since we have resolved the five stable isotopes of W\(^{180}\)W, \(^{182}\)W, \(^{184}\)W, \(^{186}\)W and the two stable isotopes of Re\(^{186}\)Re, \(^{187}\)Re in a W–25 at.\% Re alloy (see figures 3(a), (b) in Hall et al 1976). Furthermore, the results presented in §5 amply demonstrate the adequacy of the resolution of the straight TOF atom probe.

4 Computer system

The atom probe has been interfaced to a Nova 1220 minicomputer which can collect, store and analyse the mass spectrometer data. The computer system hardware consists of (i) a Data General Nova 1220 minicomputer with 32k words of memory; (ii) three Data General magnetic cassette tape transports; (iii) a Tektronix 4010 graphics display terminal and 4610 hard-copy unit; and (iv) an ASR33 Teletype. The computer system interacts with the atom probe via an Analogic 5800 series A/D converter, which is used to measure the specimen voltage, and a specially constructed interface which allows the computer to trigger the high-voltage pulse to the specimen and to read in the tofs from the digital timer. With the aid of this automated system we can presently record and analyse 600 TOF events min\(^{-1}\).

4.1 Computer program to operate the atom probe

A program called the Atom-Probe Operating System (APOS) is used when the computer is controlling the atom probe. This program is written in BASIC and ASSEMBLY languages and incorporates many interactive features which allow the operator to monitor continuously the performance of the atom probe. The principal features of this program can be described most easily by listing the sequence of events that take place in a typical experiment. After certain variables have been initialized, such as the calibration parameters, the computer initiates the pulsing of the FIM tip. As the FIM specimen is field-evaporated the voltage is slowly raised by the operator to maintain a steady pulse evaporation rate as monitored by an audio rate meter. After each pulse the computer reads in the TOF and voltage data, computes the \( m/n \) values, increments the appropriate bin of the histogram by one and then stores the data on magnetic cassette tape. When sufficient data have been accumulated in the histogram they are displayed on the graphics display terminal. The information on the cassette tape can be read back to reproduce the histogram or to produce a composition profile showing the cumulative number of atoms of a given type within a specified \( m/n \) range as a function of the total number of atoms detected.

The physical principle behind a composition profile is illustrated in figure 3. Figure 3(a) shows a FIM tip formed from a solid-solution alloy consisting of solvent A and solute B. The tip contains a precipitate rich in B; the solute atoms are denoted by the full circles. The tip-to-image intensification system distance is adjusted so that during the course of the pulsed-field evaporation of the specimen all the atoms (A and B) contained within the indicated cylindrical volume element are chemically analysed by the atom probe.

Figure 3(b) shows the corresponding composition profile: the number of B-atoms against the cumulative number of A- and B-atoms. The cumulative number of atoms is proportional to depth \( z \) since the specimen is chemically analysed by
During the course of an atom-by-atom dissection of an FIM specimen by the pulsed-field evaporation technique the atom probe determines the distribution of chemical species in an approximately cylindrical volume element of the specimen as shown in 3(a). A plot of the number of B-atoms (we consider here the case of a binary alloy consisting of A- and B-atoms) as a function of the total number of atoms (A plus B) detected yields a composition profile. The presence of a local composition variation produced by a precipitate results in a change of slope of the composition profile; this is illustrated in 3(b).

In this section we report on the chemical analysis of a number of isotopes of Mo (92Mo, 94Mo, 95Mo, 96Mo, 97Mo, 95Mo, 100Mo) and for the suppression of void formation. An FIM specimen was prepared from off-the-spool W-25 at. % Re thermocouple wire; its n/m spectrum has been previously published (Hall et al. 1976). The composition profiles for the two stable Re isotopes (186Re, 188Re) may be found in Wagner et al. (1976). Figure 3

**Figure 3**

During the course of an atom-by-atom dissection of an FIM specimen by the pulsed-field evaporation technique the atom probe determines the distribution of chemical species in an approximately cylindrical volume element of the specimen as shown in 3(a). A plot of the number of B-atoms (we consider here the case of a binary alloy consisting of A- and B-atoms) as a function of the total number of atoms (A plus B) detected yields a composition profile. The presence of a local composition variation produced by a precipitate results in a change of slope of the composition profile; this is illustrated in 3(b).

**5 Some experimental results**

In this section we report on the chemical analysis of a number of pure metals and alloys by the atom-probe technique. The materials examined included tungsten, molybdenum, tungsten–rhenium, molybdenum–titanium, molybdenum–titanium and zirconium (commonly called TzM), a special low-swelling stainless steel alloy (LSIA) and an iron-based metallic glass (Metglas 2826). The results of the experiments on these materials demonstrated that they could be chemically analysed quantitatively and that more detailed experimental investigations of irradiation-produced defects in them should be straightforward.

Before presenting the experimental results we briefly discuss the use of the word 'clustering' as it is germane to our results on alloys. In the theory of solid solutions (e.g. see Christian 1965a) the term clustering has an exact meaning. Specifically, clustering (or negative short-range order) implies that like atoms have a greater than random probability of being nearest neighbours of one another; this behaviour is indicative of a miscibility gap, at lower temperatures, on a phase diagram. Alternatively, short-range order (i.e. anti-clustering) implies that unlike atoms have a greater than random probability of being nearest neighbours of one another; this behaviour is indicative of a disorder–order transformation, at lower temperatures, on a phase diagram. Furthermore, a random solid solution will exhibit composition fluctuations and the root mean square deviation $\langle (\Delta x)^2 \rangle^{1/2}$ from the average composition (in atom fraction) of the solute (x) is given by $\sqrt{x(1-x)/N}$ where N is the total number of atoms involved in the fluctuation. Since we are dealing with small sample sizes the probability of seeing a local composition fluctuation is high and, indeed, our composition profiles do exhibit these composition fluctuations. The total sample size can be quite large; for example, it is possible to obtain a composition profile of 105 atoms. By small sample size we mean a small volume of space within the total sample volume which can contain only a single atom if so desired.

The term cluster is also used, for example, in discussing Guinier–Preston (GP) zones (e.g. see Christian 1965b). With the atom-probe technique it is possible to observe this pre-precipitation phenomenon. Finally, we come to a precipitate which represents a separate phase of the system (independent of whether it is stable or metastable). The FIM image can be used, in conjunction with the composition profile, to definitively identify a precipitate and hence to distinguish it from (a) clustering; (b) short-range order (or anti-clustering); (c) composition fluctuation; or (d) pre-precipitation clusters such as GP zones. In this section we use the term cluster to indicate any local composition fluctuation which is obviously greater than the composition fluctuations expected in a random solid solution, although, in principle, it is possible to make the distinctions enumerated above.

5.1 Pure metals (tungsten and molybdenum)

The spectra of W-9, W-4 and Mo-9 have been published earlier (Wagner, Hall and Seidman 1975, Hall et al. 1976). The spectrum of W-9 clearly shows the five stable isotopes of W (180W, 182W, 184W, 186W, 188W) and the measured isotopic abundances were in good agreement with the handbook values. In the Mo-9 spectrum we very clearly resolved the seven stable isotopes of Mo (93Mo, 94Mo, 95Mo, 96Mo, 97Mo, 98Mo, 100Mo) and we also obtained isotopic abundances which agreed very well with the handbook values (Hall et al. 1975).

5.2 Tungsten–25 at. % rhenium alloy

The results on W (see 5.1) and W–25 at. % Re will serve as a control for some in-progress experiments on fast-neutron-irradiated specimens of these same materials. Pure W exhibits considerable swelling (void formation) as a result of fast-neutron irradiation at about 0.4–0.6 of the absolute melting temperature and the addition of Re to W strongly suppresses this swelling (Mottef et al. 1975). It is our objective to determine how the Re is redistributed as a result of the fast-neutron irradiation treatment in an effort to determine the mechanism(s) for the suppression of void formation.

An FIM specimen was prepared from off-the-spool W–25 at. % Re thermocouple wire; its n/m spectrum has been previously published (Hall et al. 1976). The composition profiles for the two stable Re isotopes (185Re, 187Re) may be found in Wagner et al. (1976). This experiment demonstrated that the Re isotopes can be distinguished from the immediately adjacent W isotopes (184W, 186W). The average composition of the Re determined for the 185Re isotope was 10–6 at. % and for...
the $^{188}$Re isotope it was 14.8 at.%; hence the overall composition was 25.4 at.%. Re as determined from the average slopes of the composition profiles. The first conclusion drawn from this experiment was that a Re concentration of 25 at. % or higher could be easily detected in W. A second conclusion is that the vast majority of the Re atoms were in solid solution in this specimen; this conclusion was based on the fact that the measured Re concentration was approximately equal to the nominal composition of the alloy and also that the TIM image showed no evidence for precipitation. A third conclusion is that there was no evidence for any pre-precipitation. A fourth conclusion is that the composition profiles exhibit composition fluctuations about the average Re isotope compositions. To date we have been unable to conclude whether or not there is any evidence for short-range order (anti-clustering) obtainable from the composition profiles.

5.3 Molybdenum–(titanium) alloy
The Mo–1.0 at.% Ti alloy exhibits an enhanced swelling behaviour compared to the molybdenum specimens irradiated under identical conditions to the same fast-neutron dose (Moteff et al 1975). It is the purpose of the present experiment to determine the role played by the titanium in the swelling enhancement behaviour of neutron-irradiated Mo(Ti). It is interesting to note, by contrast, that Johnston et al (1976) have found Ti to be a particularly effective swelling inhibitor in a series of model Fe–Cr–Ni alloys.

Atom-probe FIM experiments were performed on unirradiated specimens of a Mo–1.0 at.% Ti alloy; the results will serve as a control for a series of experiments on neutron-irradiated Mo–1.0 at.% Ti. The alloy was originally swaged from re-roll stock which had been recrystallized at 1000°C and then heat-treated to 1.5 mm diameter between 815 and 980°C. A wire specimen was prepared from the 1.5 mm diameter rod by thinning it electrolytically to 0.2 mm diameter using a solution which consisted of 25 parts H$_2$SO$_4$; 175 parts CH$_3$OH (by volume). The FIM specimens were prepared by the dipping technique at 5 V ac in a solution of 1 part H$_2$SO$_4$ : 4 parts HCl : 8 parts CH$_3$OH (by volume).

The Ti–3 spectrum for the as-received Mo–1.0 at.% Ti alloy is shown in Wagner et al (1976). The five isotopes of Ti ($^{46}$Ti, $^{47}$Ti, $^{48}$Ti, $^{49}$Ti, $^{50}$Ti) are very clearly resolved from one another. The five Ti–3 isotopes present a very decisive indicator of Ti which allows us to distinguish it from oxygen; oxygen has only three isotopes ($^{16}$O, $^{17}$O, $^{18}$O) with $^{16}$O having a natural abundance of 99.8 at. % of the three O isotopes. The concentration of Ti was determined to be 0.28 at.%; this represents 28% of the nominal Ti concentration. There may also be additional Ti atoms which field-evaporate in the +2 charge state and would therefore be superimposed on the Mo–3 portion of the spectrum. However, it is emphasized that Chang and Perlmutter (1963) have shown that Mo$_2$C, TiC and ZrC precipitates can form in both Mo(Ti) and TZM. Thus the remaining 72% of the Ti may alternatively be tied up in the form of TiC precipitates which exist at a number density below the limit of detection of the TIM technique. The Ti observed was also found to be uniformly distributed throughout the alloy without any gross clustering effects. This is significant because a comparison of the present results with the results on the irradiated Mo(Ti) alloys should allow us to comment in detail on the changes produced in the spatial distribution of Ti atoms in the alloy as a result of the fast-neutron irradiation.

The Mo(Ti) spectrum was recorded with the atom probe at a background pressure of 6.9 x 10$^{-8}$ Pa at a tip temperature of 42 K. The major residual gas components were H$_2$ (6.29 x 10$^{-8}$ Pa), He (2.66 x 10$^{-10}$ Pa), CH$_3$ (2.26 x 10$^{-9}$ Pa), CO (3.19 x 10$^{-9}$ Pa) and CO$_2$ (5.32 x 10$^{-10}$ Pa). The voltage range was $V_{pc}$ = 5600–9400 V, the value of $f$ was 0.05 and the calibration parameters were $a = 1.2$, $t_0 = 0.56$ ps, $d = 2218$ mm.

5.4 Molybdenum–(titanium and zirconium) alloy (TZM)
The alloy Mo–1 at.% Ti–0.08 at.% Zr (TZM) has been found to exhibit an enhanced swelling behaviour and a very fine dislocation substructure when compared to molybdenum for fast-neutron-irradiation temperatures of less than 650°C (Eyre 1972). At present we are engaged in a study to determine the role(s) played by the Ti and Zr additions to Mo in causing this swelling enhancement. The atom-probe data on TZM presented in this section will serve as a control for our experiments on fast-neutron-irradiated TZM specimens.

The 0.2 mm diameter wire FIM specimens were cold-drawn from a 1 mm diameter rod of TZM which had been stress-relieved between 870 and 980°C. After the cold-drawing operation the wire specimens were brittle and somewhat fibrous. The TIM specimens were prepared by the dipping technique in the electropolishing solution used for the Mo–1.0 at.% Ti alloy.

Figure 4 shows a semilogarithmic plot of the $m/n$ histogram of TZM between 0 and 55 u. The peaks near 24, 32 and 48 u are associated with Mo–14, Mo–28 and Mo–32 respectively. The

![Figure 4](image-url)

Figure 4 Semilogarithmic plot of the $m/n$ spectrum for TZM. Note that the seven isotopes of Mo, the $^{90}$Zr isotope and four of the five isotopes of Ti are clearly visible. The absence of $^{46}$Ti and $^{94}$Zr peaks is not surprising since these isotopes would be expected to produce only 1 ± 1 event on a statistical basis. The Ti concentration corresponds to 0.26 at.% Ti and the Zr concentration to 0.13 at.% Zr. Note the total absence of background counts resulting from the low background pressure (6 x 10$^{-8}$ Pa).
cluster of peaks near 16 u is associated with Ti-3 (46Ti, 47Ti, 48Ti, 50Ti) and corresponds to a Ti concentration of 0.26 at.%; this represents 26% of the nominal Ti concentration. The comments made in §5.3 on the difference between the measured and the nominal Ti concentration in the Mo(Ti) alloy also apply to TZM. The peaks at 30 and 45 were H2 (5.63 with 9oZr+2 respectively and correspond to a total Zr concentration.

The spatial distribution profiles of Ti and Zr are shown in Wagner et al. (1976). The Ti atoms observed were distributed uniformly throughout the specimen and they did not exhibit any gross clustering effects. By comparison all the Zr atoms detected were contained in single cluster. This Zr cluster was detected just before the FIM tip failed and it may have contributed to the failure of the tip. These control experiments on TZM demonstrated that both the Ti and Zr alloying elements in the <0.5 at.% range could be detected in Mo.

With the exception of a few events in the range 1-6 u (which are associated with H, He and C) the spectrum shows a very clean background. The TZM spectrum was recorded with the atom-probe at a background pressure of 6 x 10^-9 Pa and at a tip temperature of 35 K. The major residual gas components were H2 (5.63 x 10^-9 Pa), CH4 (1.06 x 10^-9 Pa), CO (2.39 x 10^-9 Pa) and CO2 (4.16 x 10^-9 Pa). The voltage range was Vbc=12 200-13 300 V, the value of f was 0.05 and the calibration parameters were a=1.2, t0=0.56 μs, d=2218 mm.

5.5 Low-swelling stainless steel alloy (LS1A)

A low-swelling stainless steel alloy (LS1A) developed at the Oak Ridge National Laboratory (ORNL) by Bloom et al. (1976) has been analysed with the atom-probe FIM technique. To date we have restricted our work to unirradiated specimens of this alloy because of the high radioactivity of the neutron-irradiated specimens. LS1A contains 2-06 at.%, Si and 0-16 at.%, Ti as swelling inhibitors. It is the purpose of the present study to determine the role played by these swelling inhibitors. The material was examined in the cold-worked state after having been drawn from a 0-24 mm to a 0-20 mm diameter wire. After each drawing pass except the last one, the material was annealed at 1050°C for 15 min in an argon atmosphere. The FIM specimens were prepared by the dipping technique at 10 V DC in an electropolishing solution consisting of 33% H3PO4 in HzO.

The uncertainties were calculated from the \( \sqrt{N/N} \) values where N is the number of atoms counted.

<table>
<thead>
<tr>
<th>Element</th>
<th>Chemical analysis (atomic %)</th>
<th>Atom-probe analysis of the bulk specimen (atomic %)</th>
<th>Atom-probe analysis of a cluster (number of atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>64.0</td>
<td>62.2 ± 1.1</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>17.4</td>
<td>14.5 ± 0.5</td>
<td>0</td>
</tr>
<tr>
<td>Ni</td>
<td>12.9</td>
<td>16.2 ± 0.6</td>
<td>3</td>
</tr>
<tr>
<td>Mn</td>
<td>2.0</td>
<td>2.6 ± 0.2</td>
<td>1</td>
</tr>
<tr>
<td>Mo</td>
<td>1.0</td>
<td>1.8 ± 0.2</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>0.37</td>
<td>0.4 ± 0.1</td>
<td>2</td>
</tr>
<tr>
<td>Si</td>
<td>2.1</td>
<td>1.7 ± 0.2</td>
<td>3</td>
</tr>
<tr>
<td>Ti</td>
<td>0.16</td>
<td>0.20 ± 0.06</td>
<td>2</td>
</tr>
<tr>
<td>Other</td>
<td>0.15</td>
<td>0.5 ± 0.1</td>
<td>0</td>
</tr>
</tbody>
</table>

Totals 100.1 100.1

a The uncertainties were calculated from the \( \sqrt{N/N} \) values where N is the number of atoms counted.

Figure 5 Semilogarithmic plot of the m/z spectrum of LS1A. The main constituents (Fe, Ni, Cr) as well as the minor alloying additions with concentrations of fractions of an atomic per cent (Mn, Mo, Si, Ti) are easily detected by the atom-probe FIM technique. The average compositions determined from this histogram are listed in table 1.
Iron-based metallic glass (Metglas 2826)

A metallic glass (Metglas 2826) with a nominal composition of 40 at.\% Fe, 40 at.\% Ni, 14 at.\% P and 6 at.\% B was examined by the atom-probe technique (see Masumoto and Maddin (1975) for a review of research on metallic glasses). The experiments were performed to establish the feasibility of studying the clustering behaviour of the phosphorus and boron in this alloy. The clustering of phosphorus had been suggested as a possible mechanism for the embrittlement of this alloy following heat treatment below its crystallization temperature. Prior to the atom-probe examination the specimen was annealed at 150-170°C for about 6 h (a standard UHV bake-out of the FIM). The FIM specimens were prepared in an electropolishing solution which consisted of 4 parts ethanol: 1 part perchloric acid (by volume).

The m/n spectrum for Metglas 2826 in figure 6 shows that the various constituents can be easily identified. The composition as determined by an atom-probe analysis is 35.8±1.3 at.\% Fe, 37.1±1.3 at.\% Ni, 20.9±1.0 at.\% P and 6.2±0.5 at.\% B; the spatial distributions of B and P in this specimen are plotted in figure 7. The composition values for Fe, Ni and B are in reasonable agreement with the nominal compositions supplied by the manufacturer is incorrect for the material we used; and (2) the region of space sampled in our experiment was occupied by a cluster rich in P.

The Metglas 2826 data were recorded in the presence of 1.33×10^{-5} Pa Ne at a background pressure of 3.32×10^{-7} Pa and at a tip temperature of 63 K. The voltage range (VDC) was varied between 18 500 and 19 400 V, the value of f was 0.10 and the calibration parameters were α=1.482, t₀=56 μs, d=2231 mm.

Acknowledgments

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