THE SPRING RESEARCH AND MANUFACTURERS' ASSOCIATION

THE POSSIBLE APPLICATION OF REFRACTORY METALS AS SPRINGS

by

M. O'Malley, B.Sc.

Report No. 326

MARCH 1980

THE SPRING RESEARCH AND MANUFACTURERS' ASSOCIATION

Report No. 326

THE POSSIBLE APPLICATION OF REFRACTORY METALS AS SPRINGS

SUMMARY

Work has been carried out on springs made from molybdenum and tungsten wire, to assess their relaxation resistance, with regard to use of these materials as springs for high temperature applications. The results showed that these materials had poor relaxation resistance, and when the results were compared with the values of relaxation expected of heat resistant spring materials currently in use at similar stresses and temperatures, the molybdenum and tungsten springs suffered far more relaxation. It would thus appear that molybdenum and tungsten are unsuitable for high temperature spring applications.

Further investigations are required to assess the relaxation behaviour of the various molybdenum and tungsten alloys available. These alloys are either precipitation hardening or solid solution hardening alloys and so they should have better relaxation resistance than the pure refractory metals and should be more suitable for spring applications.

MARCH 1980

CONTENTS

Report No. 326

THE POSSIBLE APPLICATION OF REFRACTORY METALS AS SPRINGS

by

M. O'Malley B.Sc.

1. INTRODUCTION

A considerable number of springs in service at this present moment in time have to operate at elevated temperatures. Over the years, the maximum operating temperature has gradually been increased as heat resistant alloys have been introduced, until with the advent of nickel alloys e.g. Nimonic 90, Inconel X - 750 etc., the maximum permissible operating temperature has risen to become 500°C. Any attempt to use these materials much above this temperature results in massive relaxation of the springs.

The need to produce springs which could operate above this limiting temperature has led to a programme of work being carried out by the Assoication into the possible use of refractory metals as springs. These materials have, for a number of years, had high temperature applications e.g. as furnace winding elements and as lightbulb filaments. Their very high melting points (see Table I) and inherent strength at fairly high temperatures (at 600°C tungsten retains 60% of its room temperature tensile strength, molybdenum retains 45% of its room temperature tensile strength) made them a natural choice for this investigation.

2. MATERIALS INVESTIGATED

It was decided to carry out the investigation on springs made from 1.00 mm diameter molybdenum and tungsten wires. The tensile properties of both materials were obtained using the Association's Amsler multi-range vertical tensile testing machine and these are shown in Table II. The torsional propeties of the molybdenum were obtained using the Association's

Amsler vertical torsion testing machine and these are also shown in Table II. The tungsten wire could not be torsion tested using this method owing to the brittleness of the wire which tended to delaminate as the grips on the machine were tightened. The value of the rigidity modulus for tungsten, which is given in Table II, was obtained using a torsioanl pendulum (See Fig. 1). The rigidity modulus G is calculated from the following formula:-

$$G = \frac{2\pi \, ml^2 \times 10^{-3}}{3r^4} \times \frac{L}{T^2} \qquad \ldots\ldots\ldots\ldots(1)$$

Where G = modulus of rigidity, N/mm^2
m = mass of beam, kg
l = length of beam, mm
r = radius of wire, mm
L = length of wire, mm
T = time for one cycle, S

Springs were produced to the dimensions listed in Table III using a Carlson hand coiler. The molybdenum was obtained in the arc-cast condition, which is more ductile than that produced using the powder metallurgy method, and so at room temperature the molybdenum was ductile and could be coiled cold. Unfortunately, tungsten can only be obtained in the form produced by the powder metallurgy method and so, as its brittle-ductile transition temperature is above room temperature it had to be warm coiled to prevent fracture occurring. Preliminary coiling tests carried out on the tungsten showed that a temperature of 40°C was sufficient to render it coilable. This was achieved by heating the mandrel, on which the spring was to be formed, to about 60°C and then playing a stream of warm air on the tungsten wire during the coiling process.

After the springs had been coiled and end-ground, they were heat-treated. During the wire drawing process, the structure of the metals is changed and they take on a fibrous structure. This can lead to delamination problems with the materials, as seen during the torsion-testing of the tungsten, when stress is applied to them. A suitable heat treatment is therefore required to produce a more homogenous structure in the metals, and to reduce the stresses introduced during the coiling process.

The heat treatments carried out were 980°C for 1 hour in an inert atmosphere (in argon) for the molybdenum and 1100°C for 1 hour in an inert atmosphere (in argon) for the tungsten. The inert atmosphere is required to prevent oxidation of the metals.

3. EXPERIMENTAL METHOD

The investigation involved compression of the springs on Nimonic bolts to stress levels of 200, 300 and 400 N/mm^2 for the molybdenum springs, and 200, 400 and 600 N/mm^2 for the tungsten springs. (Nimonic bolts were used in the investigation as these could withstand the temperatures used in the tests without the threads seizing). The load required to stress each spring to the required level was calculated from:-

$$P = \frac{\pi d^2 \tau}{8cK} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where P = load (N)

τ = shear stress (N/mm^2)

D = mean coil diameter (mm)

d = wire diameter (mm)

c = spring index = $\frac{D}{d}$

K = Sopwith correction factor for curvature = $(c + 0.2)/(c - 1)$

The springs were then load tested to the calculated load on the Association's Probat load tester and the compressed length measured. Since the Probat has digital readouts for both the load and length measurements, which are easier to read and more accurate than the dial gauge method used previously, the amount of error arising at this stage of the investigation is reduced.

After load testing the springs were bolted down on the bolts to the measured compressed length, and placed in an oven at the required tests temperature for the test period. They were then removed, allowed to cool to room temperature and removed from the bolts. They were then re-load tested to the original bolted down length and the new load measured.

The percentage relaxation is then calculated from:-

$$Rel = \frac{Po - P}{Po} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where Rel = % Relaxation
Po = original load (N)
P = load after testing (N)

3.1 Time-Relaxation Tests

Prior to the commencement of the stress relaxation tests, time relaxation tests were carried out on both sets of springs to determine the length of time required for the springs to reach the secondary stage of relaxation.

These tests were carried out on three springs of each type at a stress level of 200 N/mm^2 and at a temperature of 300^{o}C, as at this temperature the molybdenum does not oxidise and there is no need for a protective atmosphere; also the springs take longer to reach the secondary stage of relaxation at 300^{o}C than at the intended test temperatures, ensuring that during the stress relaxation tests they will be well into this stage. From the results of these tests, the length of time required for the stress relaxation tests were determined.

3.2 Stress Relaxation Tests

Tests were carried out for 120 hours at temperatures of 500°C and 550°C for both sets of springs. Four springs were tested at each combination of stress and temperature. (24 springs in total were tested for each material). The tests on the molybdenum springs at 550°C were carried out in a nitrogen atmosphere to prevent oxidation. This precaution is necessary as the yellow oxide thus formed is toxic, and at the same time oxidation results in a loss of some of the metal thus changing the dimensions of the springs and consequently the stress applied to them.

EXPERIMENTAL RESULTS

4.1 Time Relaxation Results

The results of the tests on both types of material are given in Table IV and are illustrated in Fig. 2.

4.2 Stress Relaxation Results

The results of the tests are given in Table V and illustrated in Fig.3 for the molybdenum springs, and the results for the tungsten springs are given in Table VI and illustrated in Fig.4.

DISCUSSION OF RESULTS

The results obtained in the time relaxation tests indicated that 120 hours was a suitable length of time over which to carry out the stress relaxation tests. A large proportion (about 95%) of the relaxation suffered by the springs after longer periods of time had occurred after 120 hours.

Initially it was decided to carry out some stress relaxation tests on the molybdenum and tungsten springs at 500°C and 550°C to compare the relaxation behaviour of these springs with that of spring materials already in service at these temperatures e.g. Inconel X 750, Nimonic 90 and other heat resistant alloys. It was intended to then carry out further relaxation tests on the molybdenum and tungsten springs at higher temperatures. However, the results of these initial tests showed that the molybdenum and tungsten springs had suffered such a high degree of relaxation further testing was unlikely to yield any useful information. As molybdenum and tungsten have been used successfully for many years as furnace windings, light bulb filaments and in other high temperature applications, it would at first seem reasonable to expect them to be fairly resistant to relaxation. However, in these applications there is virtually no stress applied to the material, and consequently very little relaxation occurs.

If the values of relaxation obtained for the molybdenum and tungsten springs are compared with those which heat resistant alloys are expected to suffer under similar conditions of stress and temperature, it can easily be seen that the heat resistant alloys are far superior (See Table VII). This is probably due to the fact that most heat resistant alloys undergo precipitation hardening; a process which does not occur in pure refractory metals.

The results obtained indicate that it would be unlikely that pure molybdenum and tungsten could be used in high temperature spring applications due to their poor relaxation resistance. There are, however, available at the present time various alloys of molybdenum and tungsten which have already found openings in high temperature applications. A list of these alloys, together with their chemical compositions, is given in Table A below.

TABLE A CHEMICAL COMPOSITIONS OF THE VARIOUS ALLOYS OF MOLYBDENUM AND TUNGSTEN (1)

Alloy	Chemical Composition				
	% Ti	% Zr	% C	% W	% Mo
TZM	0.5	0.08	0.03	-	Balance
TZC	1.0	0.1	0.14	-	Balance
WZM	-	0.1	0.03	25	Balance
Mo 30W	-	-	-	30	70
Mo 50W	-	-	-	50	50

These alloys have high melting points and so are suitable for high temperature applications. Although they have body centred cubic crystal structures, they exhibit certain strengthening features; either precipitation hardening by production of a finely dispersed carbide phase (e.g. in TZM and TZC) or by a solid solution hardening process (e.g. in Mo 30W and Mo 50W) or by a combination of both these effects (e.g. in WZM). Thus dislocation movement within these materials is retarded, either by the pinning of the dislocations by precipitates or by the interaction between the dislocations and the stress fields arising around the differently sized atoms (the atomic radius of molybdenum = 1.40×10^{-10}m, the atomic radius of tungsten = 1.41×10^{-10}m(2)).

As these alloys have better creep properties than the pure refractory metals (See Table B below), then it would seem feasible to expect them to have good relaxation resistance, and so they could possibly find future applications as high temperature springs. However, work will have to be carried out to assess their relaxation behaviour.

TABLE B CREEP PROPERTIES OF REFRACTORY METALS AND ALLOYS (3)

Material	Stress required to produce rupture in 1000 hours at 1000°C (N/mm^2)
Molybdenum	90
Tungsten	140
TZM	425
TZC	425
WZM	375
Mo 30W	330
Mo 50W	350

There are, however, certain facts which may prohibit the use of these refractory metal alloys in high temperature spring applications. As molybdenum is the major constituent in all the alloys, then above 540°C there are oxidation problems, and the materials can only be used in a protective atmosphere or if coated with a suitable oxidation resistant material. Also these alloys are very expensive and very difficult to obtain and, even if they are found to have good relaxation resistance, the spring maker may find it uneconomical to use them.

6. CONCLUSIONS

1. The investigation has shown that it would not be possible to use pure molybdenum and tungsten as materials for high temperature spring applications due to their poor relaxation resistance at temperatures at which heat resistant alloys already operate.

2. The poor relaxation of molybdenum and tungsten is probably due to the fact that they do not undergo precipitation hardening, a process which the commonly used high temperature spring materials do undergo. Alloys of molybdenum and tungsten which are strengthened by either precipitation hardening or solid solution hardening could find possible applications as high temperature spring materials if their relaxation behaviour is shown to be adequate enough.

7. AREAS OF FUTURE WORK

Work should be carried out on the various alloys of molybdenum and tungsten available to assess their relaxation resistance at temperatures higher than those at which spring materials now operate. If they are found to have good relaxation resistance, then work will have to be carried out to find a suitable coating to prevent the materials oxidizing at these elevated temperatures.

8. REFERENCES

1. English, J.J. "Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum and Tungsten". Battelle Memorial Institute, DMIC Report 152 (April 28, 1961).

2. Smithells, C.J. "Metals Reference Book, Volume 1". Butterworths, 1967.

3. "Engineering Properties of Molybdenum and Molybdenum Alloys", DMIC Report 190.

4. Metals Handbook, Properties and Selection of Metals", 8th Edition, American Society for Metals, 1961.

5. Graves, G.B. "The stress-relaxation Properties of Nimonic 90 and Inconel X - 750 Helical Compression Springs". SRAMA Report No. 152.

6. Graves, G.B. and Key T. "The Stress Temperature Relaxation Properties of some High Temperature and Corrosion Resistant Materials". SRAMA Report No. 194.

TABLE I MELTING POINTS OF THE REFRACTORY METALS (4)

Material	Melting point °C
Molybdenum	2607
Tantalum	2996
Tungsten	3377

TABLE II MECHANICAL PROPERTIES OF MATERIALS INVESTIGATED IN THE AS RECEIVED CONDITION

Material	Tensile Properties					Torsional Properties			
	R_m N/mm^2	L of P N/mm^2	$R_{p0.05}$ N/mm^2	$R_{p0.1}$ N/mm^2	$R_{p0.2}$ N/mm^2	L of P N/mm^2	0.1% PS N/mm^2	0.3% PS N/mm^2	G x 10^4 N/mm^2
Molybdenum	1455	650	915	1020	1140	335	490	555	10.37
Tungsten	1930	1005	1630	1780	1855	-	-	-	14.44

TABLE III SPRING DESIGN AND DIMENSIONS

Spring Parameter	Magnitude	
	for molybdenum springs	for tungsten springs
Wire diameter (mm)	1.0	1.0
Coil diameter (mm)	7.5	7.5
Total coils	7.5	7.5
Active coils	5.5	5.5
Solid stress = 70% UTS (N/mm^2)	1020	1350
Free length after heat treatment and end grinding (mm)	15.0	17.7

TABLE IV TIME-RELAXATION RESULTS FOR MOLYBDENUM AND TUNGSTEN SPRINGS AT 200N/mm^2 AND 300°C

Material	Spring number	% relaxation after						
		24 hours	48 hours	72 hours	96 hours	120 hours	144 hours	168 hours
Molybdenum	1	6.6	8.6	9.1	10.6	10.8	11.0	11.0
	2	5.9	7.5	8.4	9.8	10.2	10.6	10.7
	3	6.8	8.2	9.4	10.7	10.9	11.0	11.1
Tungsten	1	4.2	4.7	5.0	6.4	6.5	6.6	6.7
	2	3.7	4.2	4.6	5.4	6.0	6.3	6.6
	3	4.3	4.7	5.1	6.0	6.3	6.5	6.6

TABLE V STRESS-RELAXATION RESULTS OF MOLYBDENUM SPRINGS AFTER 120 HOURS

Test temperature °C	% relaxation at stresses of		
	200 N/mm^2	300 N/mm^2	400 N/mm^2
500	20.7	39.4	53.5
	27.4	41.0	55.9
	23.6	44.8	50.7
	28.3	42.4	49.7
550	40.6	51.9	57.1
	40.7	49.8	59.9
	41.1	50.3	56.0
	40.6	51.4	54.2

TABLE VI STRESS-RELAXATION RESULTS OF TUNGSTEN SPRINGS AFTER 120 HOURS

Test temperature °C	% relaxation at stresses of		
	200 N/mm^2	400 N/mm^2	600 N/mm^2
500	13.6	30.8	44.4
	10.1	31.8	44.4
	11.6	33.7	46.8
	12.7	29.3	46.1
550	19.3	43.6	54.4
	21.7	42.8	52.6
	20.6	43.2	51.6
	23.9	43.4	47.9

TABLE VII COMPARISON OF RELAXATION BEHAVIOUR OF VARIOUS MATERIALS AT 500°C AND 550°C

Material	Temperature °C	% Relaxation at stresses of			
		200 N/mm^2	300 N/mm^2	400 N/mm^2	600 N/mm^2
Molybdenum*	500	25.0	41.9	52.5	-
	550	40.8	50.9	56.8	-
Tungsten*	500	12.0	-	31.4	45.4
	550	21.4	-	43.3	51.6
Inconel X750+	500	4.0	5.7	7.9	15.3
	550	6.6	9.2	12.7	24.5
Nimonic 90+	500	5.1	6.0	9.0	15.8
	550	8.2	11.5	16.1	31.8
A 286[†]	500	8.4	16.0	11.9	17.0
	550	13.5	17.9	23.6	41.0
Rene 41[†]	500	6.4	6.6	6.9	7.6
	550	10.5	12.0	13.7	17.9
Waspaloy[†]	500	4.0	4.7	5.6	7.7
	550	8.5	10.2	12.2	17.4

* Mean values of experimental data

[+] Values obtained by interpolation of results of work carried out by G.B. Graves(5)

[†] Values obtained by interpolation of results of work carried out by G.B. Graves and T. Key(6)

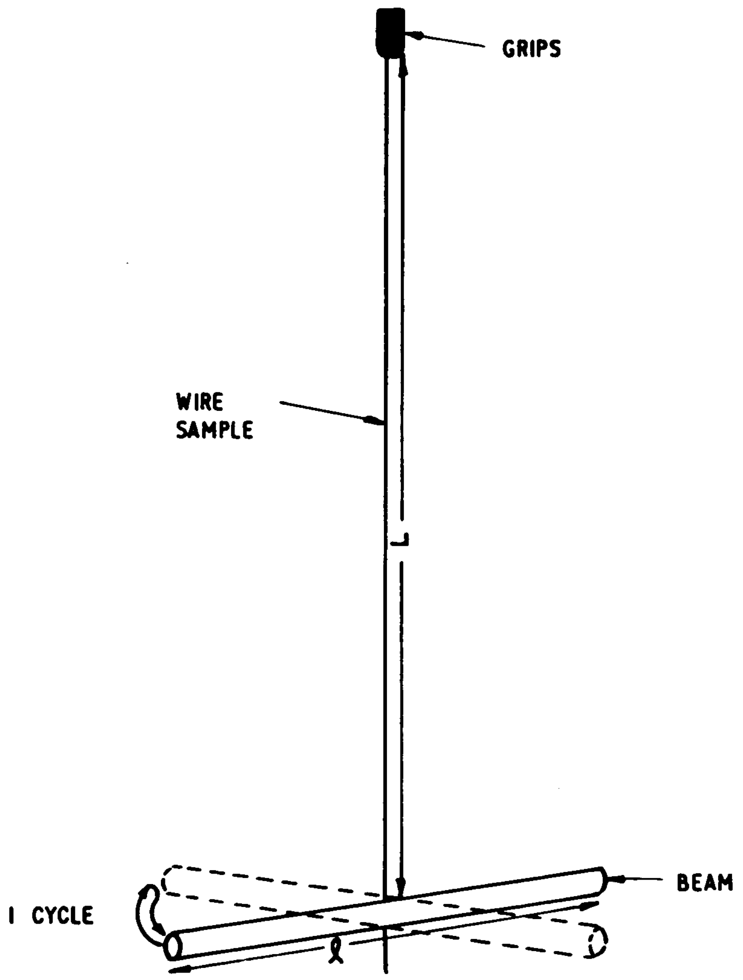

FIG. I. TORSIONAL PENDULUM APPARATUS.

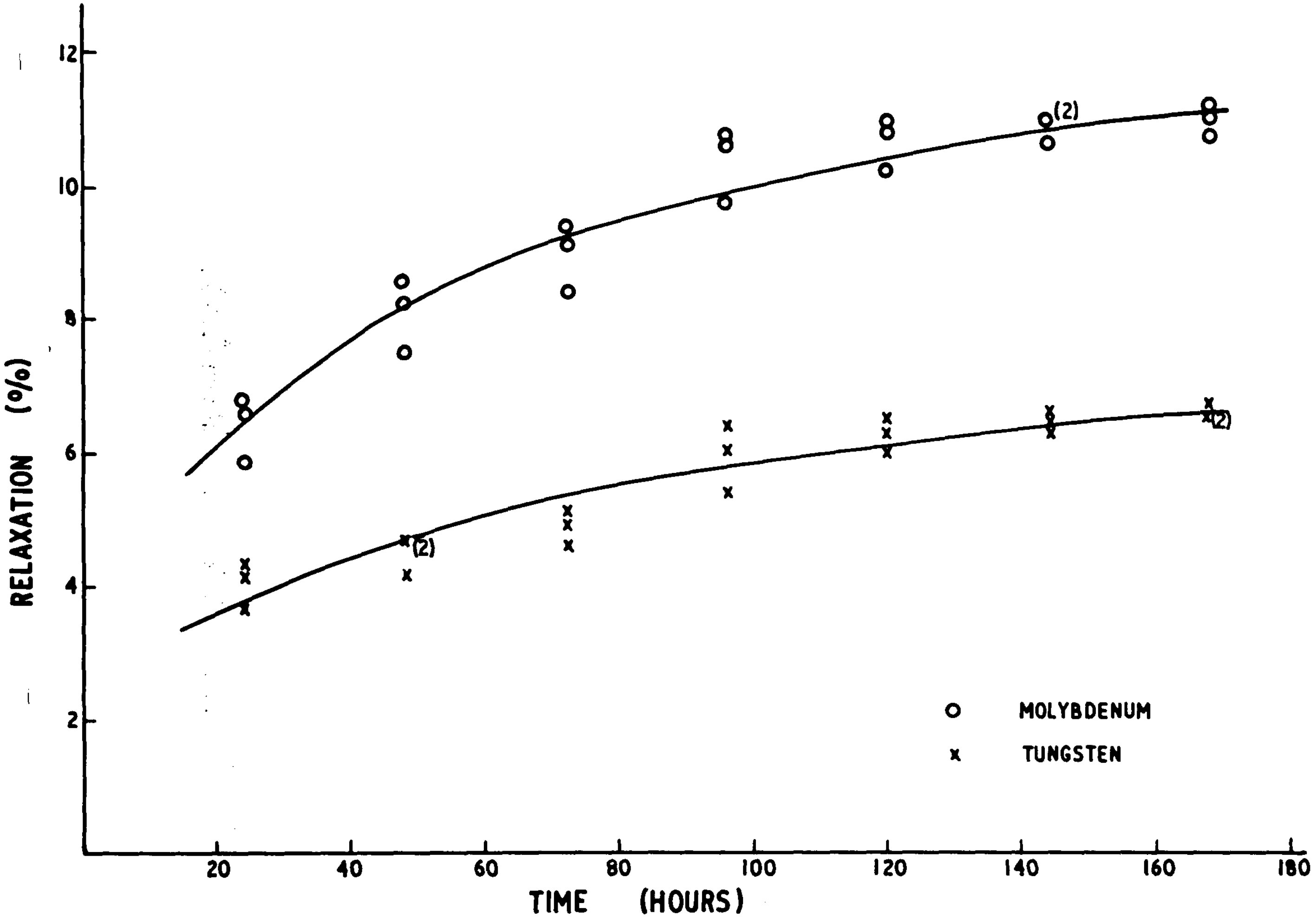

FIG. 2 TIME - RELAXATION RESULTS FOR MOLYBDENUM AND TUNGSTEN SPRINGS AT 200 N/mm² AND 300° C.

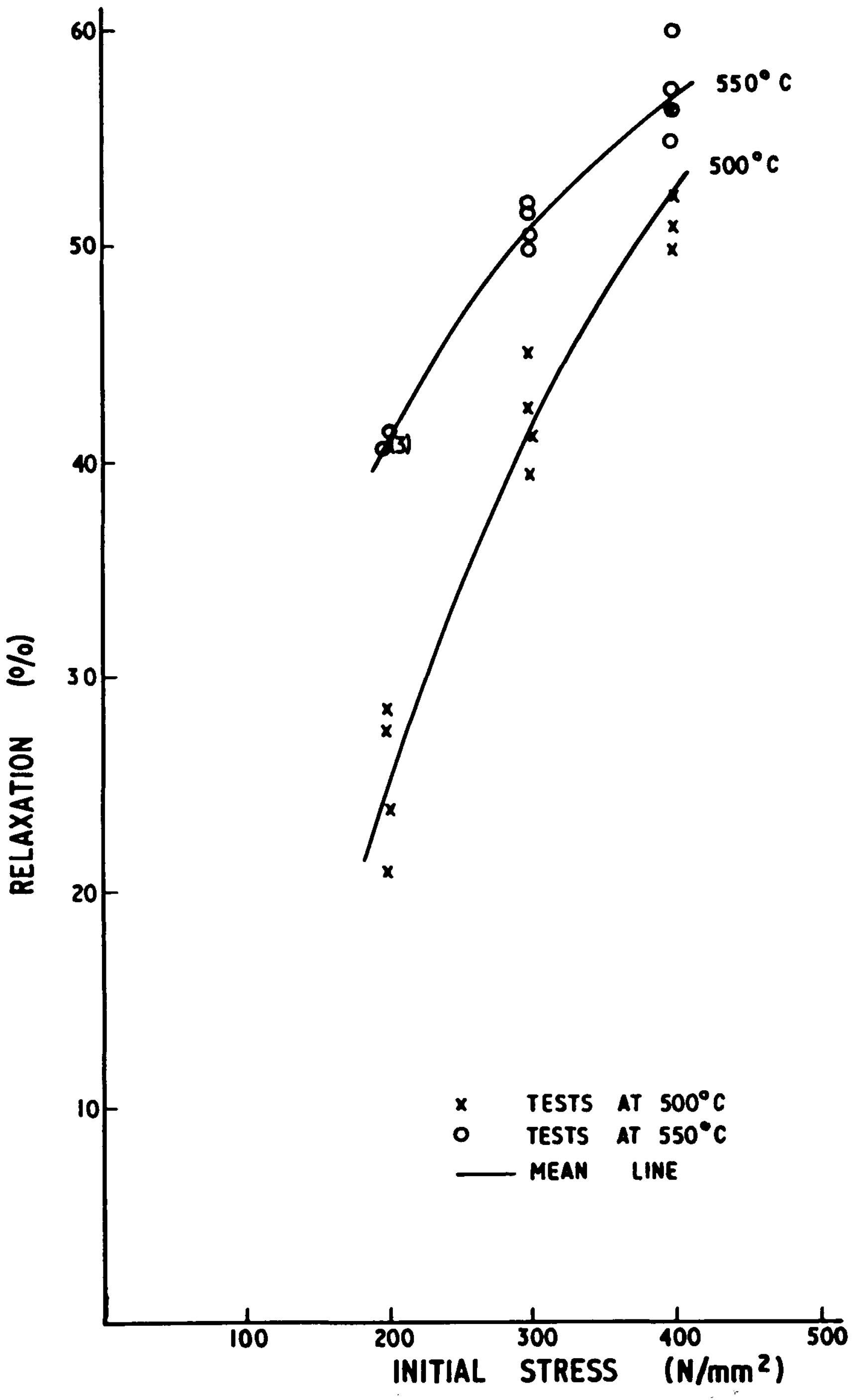

FIG. 3 RELAXATION RESULTS OF MOLYBDENUM SPRINGS AFTER 120 HOURS.

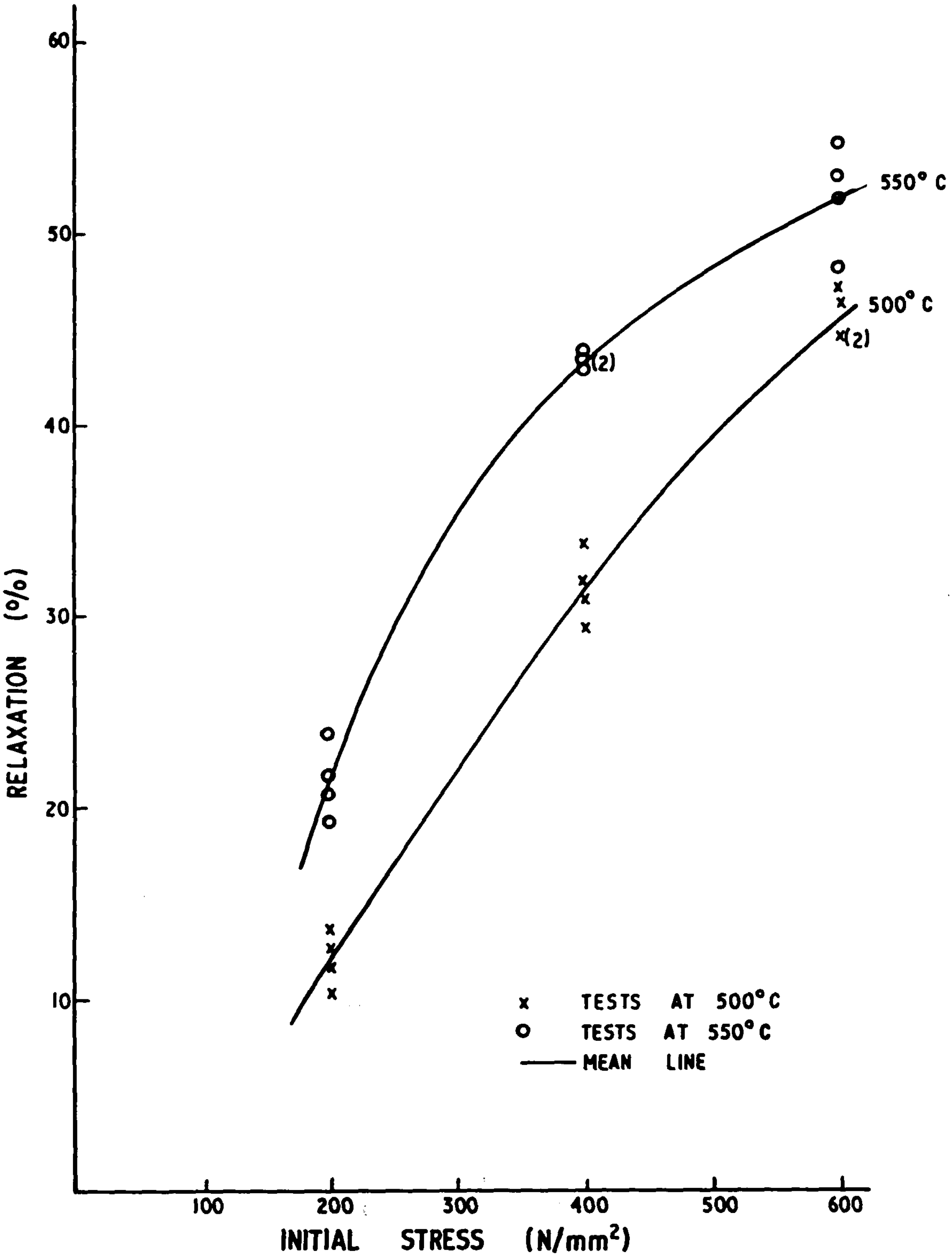

FIG. 4. RELAXATION RESULTS OF TUNGSTEN SPRINGS AFTER 120 HOURS.