THE PREPARATION AND TESTING OF Nb-Zr AND Nb-ZrO$_2$ SINGLE CRYSTALS FOR DEFORMATION STUDIES

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ABSTRACT

The difficulties to obtain adequate single crystals of Nb-Zr and Nb-ZrO$_2$ alloys for deformation studies are discussed. Low-temperature internal oxidation of Nb-Zr alloys followed by ageing at higher temperatures resulted in the precipitation of ZrO$_2$ particles. However, the effect of this treatment on the particle size and distribution and on the crystallographic structure of the particle was not completely understood. Compression tests in the temperature range 4.2K to 373K showed a small effect of zirconia particles on the mechanical properties of Nb-Zr solid solutions and a significative effect of the amount of oxygen remaining in solid solution after the oxidation treatment.

1. INTRODUCTION

Body-centred-cubic metals usually have a much larger temperature dependence of the macroscopic yield stress than metals with close-packed structures and this characteristic generated a great deal of controversy about the intrinsic or extrinsic nature of the low temperature strength[1]. Tests on very pure crystals and crystals containing controlled amounts of interstitial impurities[2,3] have shown that although interstitial impurity atoms do have an effect on some of the mechanical properties of bcc metals, there is also a strong intrinsic resistence to

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deformation related to the Peierls stress. But these experiments, also revealed other important intrinsic characteristics of bcc metals including a strong dependence of the flow stress on orientation, asymmetry of slip for glide on {112} planes, anomalous slip, a different mobility of screw and non-screw dislocations and the fact that some solutes harden the base metal at high temperatures and soften it at low temperatures[4]. Results of atomistic calculations of the core structure of a screw dislocation[5] have confirmed that the large Peierls stress for screw dislocation motion can be explained by the particular geometry of the core of screw dislocations in bcc metals. This large Peierls stress should led to different dislocation/particle behaviour and/or effects on the yield and flow stresses in bcc metals and these possibilities make the study of such alloys extremely interesting from the fundamental point of view. Furthermore, few studies on bcc single crystal alloys containing dispersion of particles have been reported[6-8] and results on polycrystal alloys with potential comercial use are often contradictory[9-14].

In the present paper difficulties in the preparation of Nb-Zr and Nb-ZrO$_2$ single crystals are discussed, and also some results of mechanical tests on these alloys in the temperature range of 4.2K to 373K are presented.

2. EXPERIMENTAL PROCEDURE

Niobium alloy single crystals were grown in a floating-zone electron-beam apparatus by melting together Nb rods and Zr wires of appropriate diameters. Initially, three passes were given at a zone speed of 300mm/hour. For the fourth and final pass the crystals were seeded and to obtain single crystals the growth rate

had to be reduced with increasing Zr content. Alloys containing
0.1wt% zirconium were grown at 300mm/hour whereas for other alloys
(higher zirconium contents) the growth rate was kept below
30mm/hour to prevent reseeding of the crystal rod.

After growth all crystals had their orientations checked
using the conventional back reflection Laue technique. After being
centreless ground to 3.1mm and chemically polished to 3.05mm
diameter the crystals were annealed in an ultra-high vacuum (UHV)
furnace at temperatures very close to the melting point. Heating
was carried out by passing a heavy current (-230 Amp) through the
specimen and before terminating the anneal the vacuum always
reached at least $1x10^{-10}$mbar. Chemical analyses of the alloys were
done either after growth or after the UHV annealing by X-ray
microanalysis; a Cameca Camebax with a wavelength dispersive
spectrometer was used.

Crystals to be internally oxidised were given a further
treatment in the same furnace. After cooling, the temperature was
raised again in the range 1073K to 1473K and oxygen bled in for
periods of 40 to 70 hours. The oxygen penetration into the rods
were monitored by measurements of the Vickers hardness numbers over
the cross section. Precipitation and growth of zirconia particles
were completed by turning off the oxygen supply and raising the
temperature to between 1673K and 1973K for periods of 1 to 10
hours. The microstructures of the substitutional alloys and of the
precipitation alloys were always checked using transmission
electron microscopy (TEM).

Compression specimens, -9mm long were cut from the
treated rod using a silicon carbide slitting wheel and jig. After
being ground to right cylinders on abrasive papers the specimens
are chemically polished to remove surface damage. Compression

tests were performed in two machines; one for temperatures in the
range 373K and 77K and the other, a gas-flow cryostat machine which
could cool the specimens down to liquid helium temperature[3].
During the tests, inversions of strain-rate by a factor of 10, from
the basic strain-rate of 1.2×10^{-4} s^{-1} were done. Temperature change
tests were also done allowing the thermal component of the flow
stress to be measured.

Oriented slices for TEM observations were cut 1mm thick,
ground on abrasive paper using shims and then chemically polished
to produce discs -0.15mm thick. Final polishing was done with a
Tenupol apparatus using 15% H_2SO_4 in methanol as electrolyte at
230K and a potential of 40 volts.

3. RESULTS AND DISCUSSION

Our first attempts to obtain single crystals of bcc alloys
containing precipitate particles were made using the Nb-Ti-N
system. However, no single crystals of Nb-Ti alloys were ever
obtained because of difficulties in matching the low zone speed
required for single crystal growth, with the rate of evaporation of
titanium. Loss of titanium was so high that in some cases the
molten zone re-solidified. A new system, Nb-Zr-O was then choosen
for the work. However, the control of the particle size and
distribution and the identification of the crystallographic
structure of the precipitate particles proved to be also a
difficult task for this system as may be inferred from the
confusing reports existing in the literature. The technique of
high temperature doping followed by rapid cooling and ageing at a
lower temperature could not be used in these alloys because of the
very low solid solubility limit of oxygen and zirconium in niobium
even at high temperatures[15]. Low temperature internal oxidation

followed by an ageing treatment at a high temperature was then made and the conditions of some heat treatments are shown in Table 1. During the oxidation treatment, very fine semi-coherent precipitate particles 100A across were formed mainly when the partial pressure of oxygen was relatively high. The subsequent short ageing treatment completed the precipitation and growth of zirconia particles and also allowed any surplus oxygen to diffuse out of the sample.

Table 1. Zirconium content (in weight %), conditions of
internal oxidation and ageing and Vickers hardness
(HVc) of some Nb-Zr and Nb-ZrO$_2$ single crystals.

Crystal	% Zr	Internal Oxidation			Ageing			HVc Kg/mm^2
		TK	p(mbar)	t/ hκ	TK	p(mbar)	t/ hκ	
435	1.42±0.35	1273	2x10^{-7}	70	-	-	-	102±03
437	1.48±0.14	1373	6x10^{-7}	27	-	-	-	94±10
440	0.09±0.04	1273	8x10^{-7}	71	1823	<1x10^{-8}	01	243±08
	1.03±0.09	1273	8x10^{-7}	7	1973	<1x10^{-8}	01	224±21
443	0.55±0.12	1273	5x10^{-7}	44	1973	<2x10^{-8}	08	76±02
445	0.12±0.04	1273	4x10^{-7}	44	1973	<8x10^{-8}	01	89±03
451	0.42±0.10	1173	1x10^{-6}	4?	1773	<1x10^{-8}	04	184±02
455	0.51±0.19	-	-	-	-	-	-	-

Contradictory results from different crystals were observed, with the interparticle distance decreasing with ageing time in some cases and increasing in others. Also, after internal oxidation the microstructure in some crystals was very heterogeneous and examples are shown in Figure 1. The common feature of these two samples is the low amount of oxygen introduced during the oxygenation process due to a low partial pressure of

oxygen in one case (crystal 435) and a short time of treatment in
the other (crystal 437). It was not possible to conclude whether
these microstructures reflected only the initial stage of
precipitation or some kind of zirconium segregation. However, after
71 hours at 1273K and a pressure of $5x10^{-7}$ mbar, a different piece
of crystal 437 showed a homogeneous microstructure, which suggests
that zirconium segregation was unlikely.

Crystal 440 was used for checking the effect of zirconium
content on the microstructure after internal oxidation and ageing.
This single crystal was grown with different amounts of zirconium
in each half. After internal oxidation the part containing less
zirconium (0.09 wt% Zr) showed larger particles and greater
interparticle distances. After a short time ageing (1 hour at
1823K) the particle size apparently decreased in both halves, being
smaller in the half containing more zirconium. The similar Vickers
hardness values in both halves of this crystal (Table 1), indicates
that oxygen remaining in solid solution may have a stronger effect
than the particles on the mechanical properties of these alloys.
This is consistent with the significant drop in the hardness value
observed after a further anneal at 1973K, i.e. it is most likely
due to loss of oxygen by degassing the matrix. Therefore, great
care is necessary in interpreting hardness measurements and
relating the values to ageing parameters in this system.

For subsequent treatments a shorter time for oxygenation
was used and as a consequence less oxygen was introduced into the
sample (shown by the hardness numbers values). Most of these
crystals showed a relatively uniform structure and they were used
for a TEM study of deformed crystals[16]. Figures 2(a) and 2(b)
show examples of structures observed for some of these crystals.
In general, low zirconium crystals had rod-shaped precipitates

with a square cross-section. Fig. 2(a), and crystals with zirconium
content greater than 0.5 wt% had precipitates in the form of cubes,
Fig. 2(b).

Pure ZrO_2 exists in three different crystallographic
forms, depending on temperature: cubic above -2470K, tetragonal
between -2470K and -1270K and monoclinic below -1270K. However
zirconia particles in a ceramic or metal matrix have been reported
to have also a metastable tetragonal or cubic structure. In a Nb
matrix the three crystallographic forms have all been observed[12-14]
and in at least one case the observed structures were thought to
be stabilized by alloying elements[17]. The cubic form of zirconia
was found to be the most likely structure in the alloys containing
the small semi-coherent particles[18]. Results of selected area
diffraction from samples containing the larger particles have shown
that for both shapes of particles (cubic and rod shapes) monoclinic
form could be excluded in most of the cases and that the most
likely particle structure is tetragonal rather than cubic. It is
then difficult to explain why is the cubic and not the monoclinic
structure stable after the internal oxidation at the relatively low
temperature and which kind of transformation can result in the
tetragonal structure observed after the ageing at higher
temperature. Elastic constraints by the Nb matrix can be
responsible, in principle, for the observed structures since a
large local volume increase should accompany the precipitation of
zirconia. Micrographs of suitably oriented foils did show coherency
strains associated with the small cubic particles but not around
the large tetragonal particles. Furthermore, the microprobe
analysis of the large particles (detection limit 40ppm) did not
reveal any Nb and this result indicates that stabilization of the
tetragonal structure by foreign elements is improbable.

Mechanical tests on these alloys have also shown surprising results. The shear yield stress versus temperature curves for a solid solution alloy (455) and alloys containing uniform (443) and non-uniform distribution of precipitates (451) are shown in Figure 3. The effect of the zirconia particles on the yield stress behaviour of Nb-Zr alloys was very small, however, the alloy containing non-uniform distribution of particles showed a much stronger temperature dependence of the yield stress than the other alloy crystals.

The thermal component of the flow str... ...tained through temperature change tests in which the sample was deformed a limited amount at one temperature, unloaded and then redeformed at a lower temperature. Figure 4 shows the thermal component of the flow stress versus temperature curves for the same group of alloys. The temperature dependences of the thermal stress were almost indistinguishable between crystals 455 and 443. Again, crystal 451 showed a much stronger temperature dependence than the solid solution and the alloy with uniform precipitation.

The results of Figures 4 and 5 suggest that zirconia particles have little effect on the mechanical properties of these Nb alloys and that a large effect exist due to oxygen in solid solution. The values of the yield stress and flow stress obtained for crystal 451 cannot be associated with the non-uniform precipitation of zirconia particles but this crystal is expected to contain higher amounts of oxygen remaining in solid solution, given the internal oxidation at higher partial pressure of oxygen and the lower temperature of ageing.

Further evidence of the small effect of zirconia particles in the deformation behaviour of Nb alloys can be obtained with thermal activated analysis. The activation volume is obtained from

the strain-rate sensitivity and is given by $v^* = KT/(\partial\sigma/\partial\ln\dot{\gamma})$. Figure 5 shows the variation in activation volume with the thermal component of the flow stress for the same group of alloys. The values obtained for the various alloys cannot be distinguished from each other and the low values of v^* for high thermal stress suggest that as in pure bcc metals only a short length of dislocation line is involved in the activation process. This means that the basic deformation mechanism observed in pure $Nb^{(3)}$ is not changed by solid solution nor by the presence of precipitate particles. It is the low mobility of screw dislocations which controls the rate of plastic deformation at low temperatures for pure bcc metals and alloys.

4. CONCLUSIONS

Several difficulties are associated with the preparation of Nb single crystal alloys containing precipitates of ZrO_2. Although precipitation occurs after low temperature internal oxidation of Nb-Zr alloys, no adequate control of the particle size and distribution could be obtained.

The presence of precipitate particles had very little effect on the temperature dependences of the yield and thermal stress; a stronger effect on these dependences was caused by oxygen remaining in solid solution after the oxidation treatments. The results of the thermal activation analysis suggested that the basic mechanism of deformation for bcc metals at low temperatures is not affected by solid solutions or by precipitate particles.

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RESUMO

As dificuldades para obtenção de monocristais de ligas de Nb-Zr e de Nb-ZrO$_2$, adequados para estudos de deformação, são discutidas neste trabalho. Tratamentos térmicos de oxidação interna nas ligas de Nb-Zr seguido de envelhecimento em temperaturas mais elevadas resultaram na precipitação de partículas de ZrO$_2$. Entretanto o efeito destes tratamentos sobre o tamanho e distribuição das partículas e sobre sua estrutura cristalográfica não pode ser completamente entendido. Testes de compressão na faixa de temperatura de 4.2K a 373K mostraram que os precipitados de zircônia tem um efeito insignificante sobre as propriedades mecânicas das ligas de Nb-Zr e que existe um efeito significativo nestas propriedades devido ao teor de oxigênio remanescente em solução sólida após o tratamento de oxidação interna.
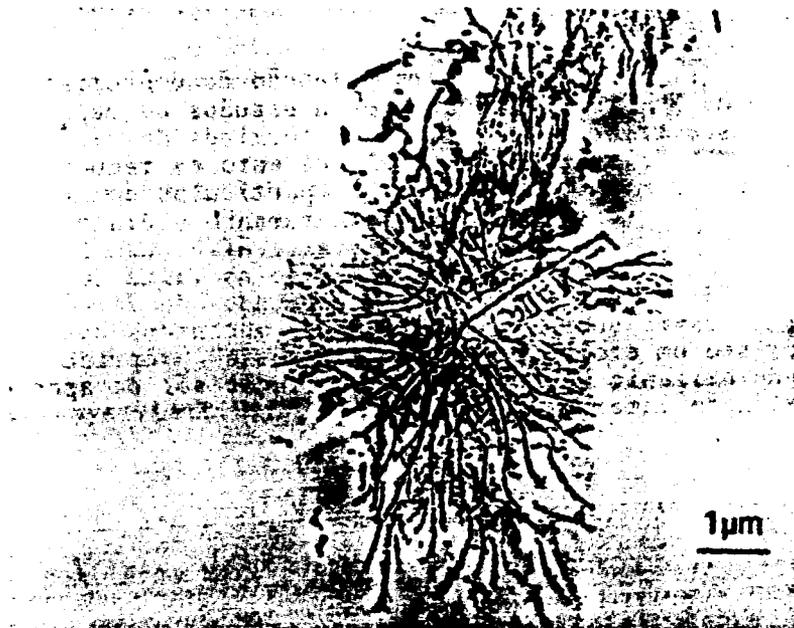
(a)
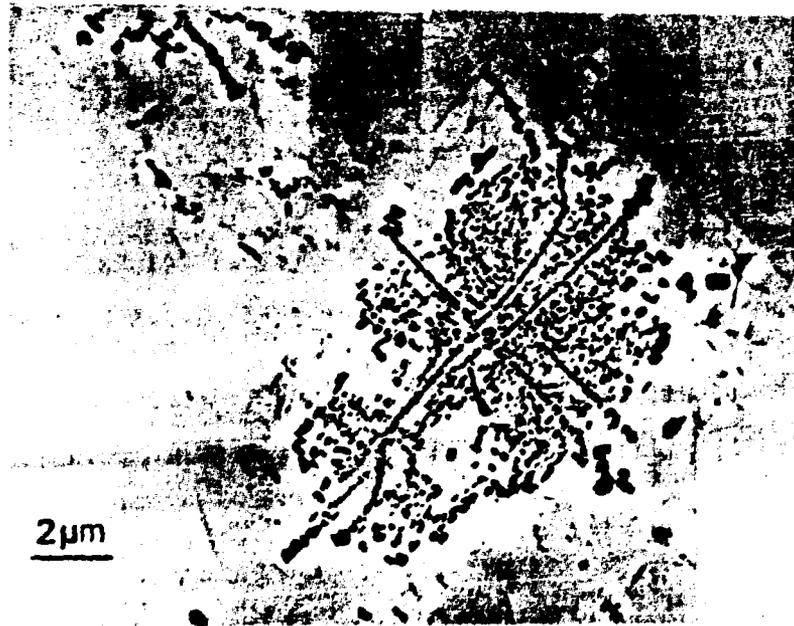
(b)

Figure 1. Heterogeneous microstructures observed by TEM
after internal oxidation of crystal 435 and 437,
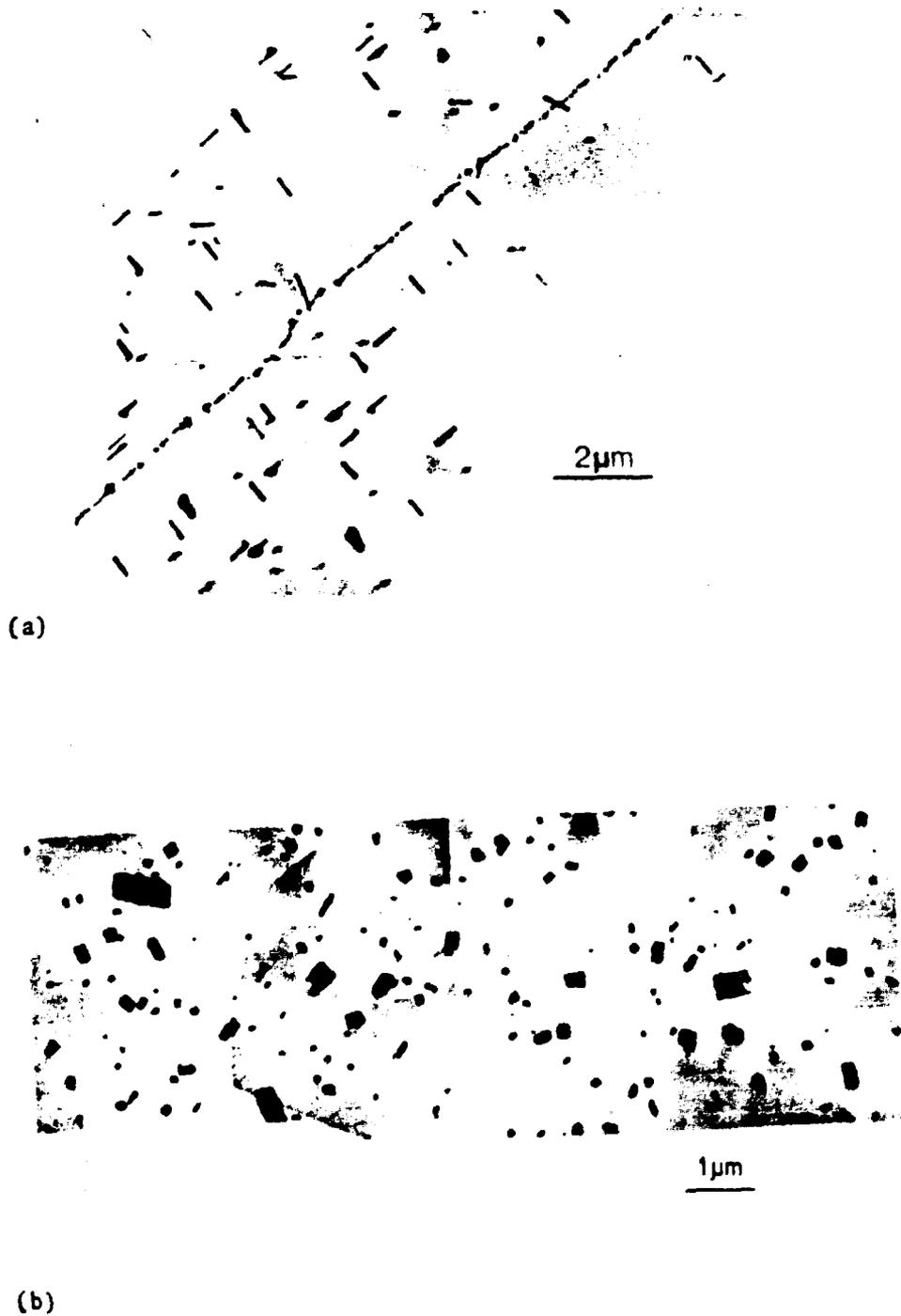(a) and (b) respectively.

(a)

(b)

Figure 2. Microstructures observed by TEM of crystals 443 and
445 after internal oxidation and ageing. (a) is
typical of high Zr content crystals (443) and (b) is
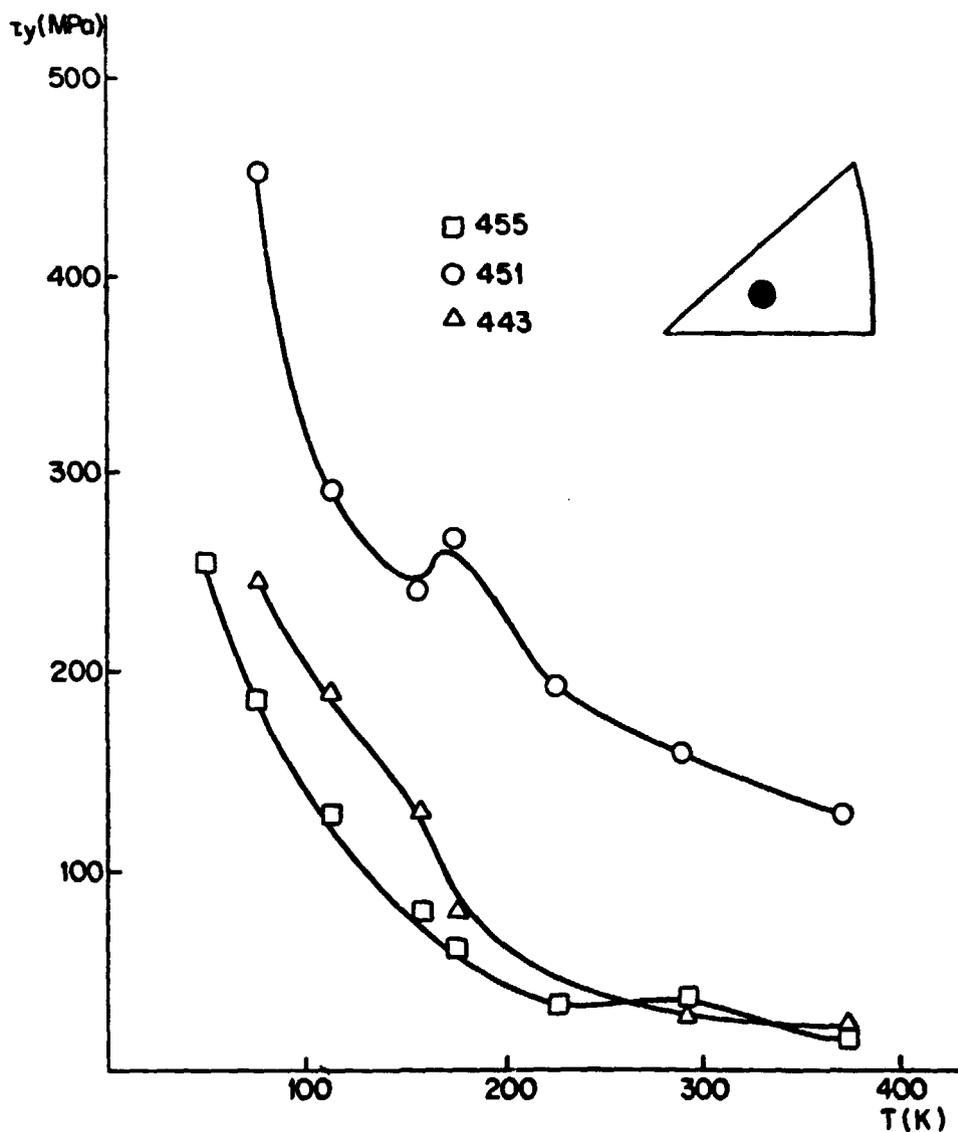typical of low Zr content crystals (445).

Figure 3. Shear yield stress vs temperature curves a for solid
solution alloy (455) and alloys containing uniform
(443) and non-uniform (451) distribution of
particles. The standard triangle indicates the
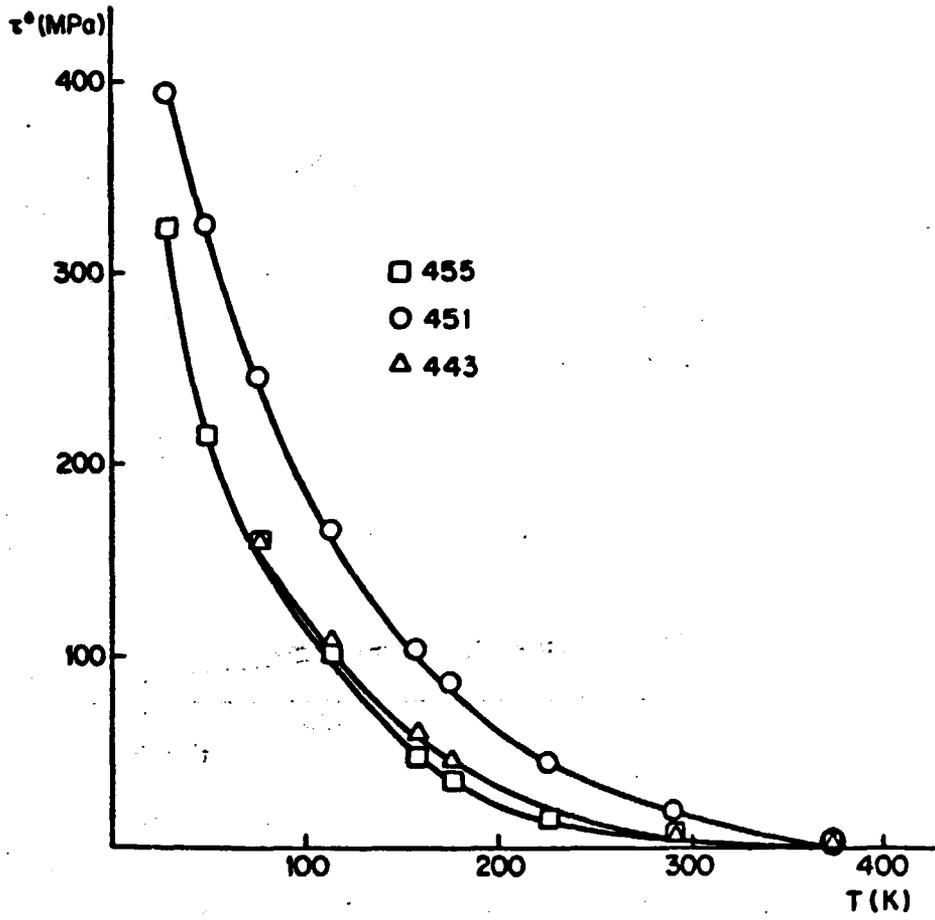orientation of all crystals.

Figure 4. Thermal component of the flow stress vs
temperature for the same group of alloys as in
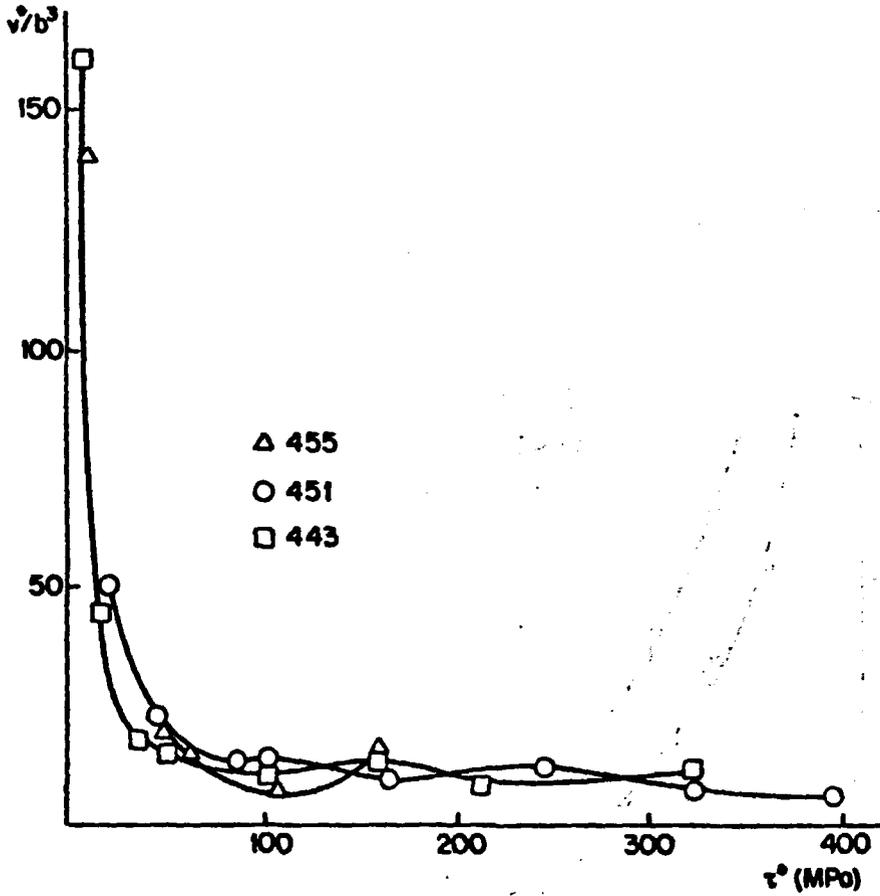the previous figure.

Figure 5. Activation volume vs thermal stress curves for the same alloys, i.e., a solid solution alloy (455) and alloys with homogeneous (443) and heterogeneous (451) microstructures.