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Copper Zirconium alloys

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Abstract
Because of the toxicity of copper alloyed with beryllium customers with aware of the environment are looking for springs with material without beryllium. For applications with high conductivity demands copper alloyed with zirconium can be a possibility, values up to 93 % IACS are reported. Ultimate tensile strength of 600 MPa is specified by the material manufacturers. The mechanical strength of a CuCr1Zr grade wire with diameter 1,5 mm was investigated and the results presented. Compression coil springs was manufactured and figures from pre-stressing behaviour and residual stresses are presented. Test was also made of different stress relief temperatures. The relaxation and fatigue strength of CuCr1Zr grade coil springs was also investigated.

Content

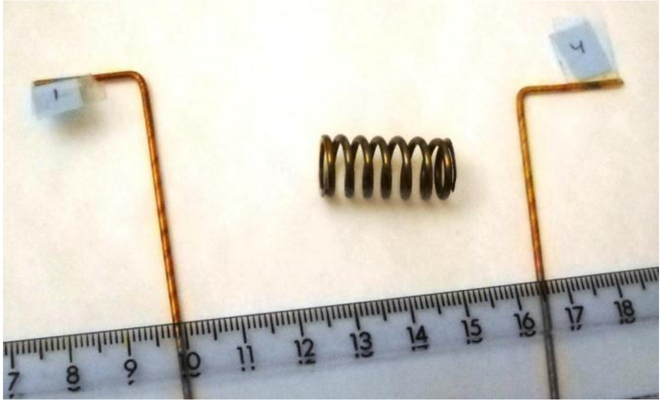
1/ Introduction
Because of the toxicity of copper alloyed with beryllium customers with aware of the environment are looking for springs made from copper zirconium alloy without beryllium. For some applications high conductivity is required and copper alloyed with zirconium can be a possible material for the springs. Some grades of this type are available on the market both as wire and strip. In this report is presented copper zirconium alloy sample investigation results and the results from literature studies.

2/ Material sample and the tests
Spring hard CuCr1Zr wire, diameter 1,50 +/- 0,02 mm and UTS 650 MPa was used for this investigations. Following parameters was tested, UTS, Rp0,2, A_{50}, Z and surface quality. Compression spring was designed, manufactured and tested regarding, shear elastic limit, plastic deformation at pre-stressing, relaxation at 25 and 200 ^{o}C and fatigue strength.
The compression springs manufacturing operations of was, coiling, stress relive, end cutting, grinding and pre-stressing. The pre-stressing was made to block length and the springs were hold there for 30 seconds. On the picture below are compression spring no.10 and two twisted wire samples photographed.

The compression spring design was following:

Dt	Di	Dm	Dy	Nv	Nt	Lo	L_{block}
1,51	8,5	10,0	11,5	5,7	7,2	23,7	11,1

Ends closed and grinded



3/ Grades

At present some grades of copper alloyed with zirconium is available on the market. Hardness and strength are lower than for BeCu alloys, but they CuZr alloys have lower impurity content, higher electrical conductivity, high ductility, resistance to softening at elevated temperatures and they also avoid the health hazards associated with BeCu. The addition of 0.15% zirconium (Zr) results in a heat treatable copper alloy which may be solution treated and subsequently aged to produce desirable properties. Zr increases softening temperatures and increases life at higher working temperatures. Depending on the application, different tempers (solution annealed, age hardened, cold worked etc.) can be defined. The oxygen content is normally not specified, but is particularly important and the content should be below 0.02%. When copper is molten it normally picks up some hydrogen, hydrogen have embrittelment effect on most copper alloys and must be controlled by the material manufacturer. Following table show present grade standards.

note /* Cu value includes Ag
note /** Cu + named elements

Grades		Chemical comp. %				
UNS	EN number	Cu/*	Cr	Zr	sum./**	others
--	CuZr, no.2.1580, CW120C	rem.	--	0,15	--	max. 0,2
C15000		min.99,8	--	0,1-0,2	min.99,9	--
C18150		rem.	0,5-1,5	0,05-0,25	min.99,7	--
--	CuCr1Zr, no.2.1293, CW106C	rem.	0,5-1,2	0,03-0,3	--	--

The best conductivity values are obtained with the material after full solution and precipitation heat treatments. For optimum mechanical properties these alloys are usually cold worked while the material is in the solution treated state. For the highest tensile properties further cold work can be carried out after precipitation heat treatment (ageing). Precipitation heat treatment need surprisingly high temperature (900-925 ^{o}C) and is made by the material manufacturer. Also the ageing is made at rather high temperature (400-425 ^{o}C) normally made by the material manufacturer. Liquidus for C15000 types is 1080 and solidus 980, for C 18150 types it is 1080 and 1070 ^{o}C.

4/ Conductivity

On a wire sample length of 10235 mm was the resistance (ohm) measured with a Kelvin four wire instrument. The result was 118,957 mΩ the conductivity was calculated to 48 Sm/mm2 which correspond well with data from the manufacturers. In the following table is published conductivity data from manufacturers presented.

note /* E C = electrical conductivity at 20 ^{o}C
note /** T C Thermal conductivity

Grades		EC	EC, Mega	TC, Btuxft/	TC
UNS	EN number	%IACS	Siemens/cm	(hrxft^{2}xF^{o})	W/mxK^{o}
--	CuZr, no.2.1580, CW120C	90	>0,50	---	320
C15000		93	0,544	212,0	366,9
C18150		80	0,464	187,0	323,9
--	CuCr1Zr, no.2.1293, CW106C	75	0,43-0,50	---	320

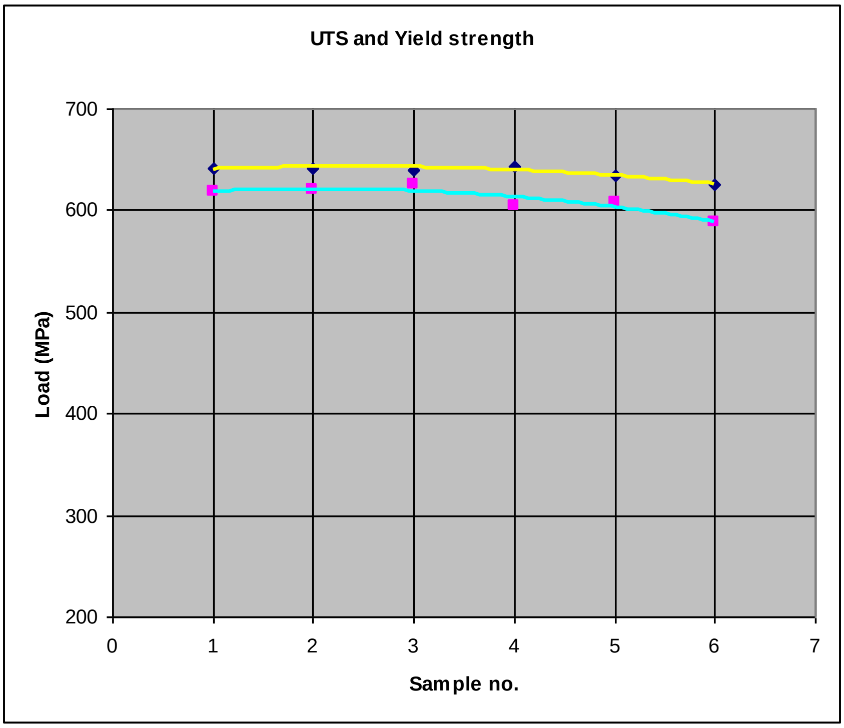
The grade C15000 has very good conductivity properties at cryogenic temperatures.

5/ Mechanical properties

Tensile test of the wire samples 1,51 mm at 22 ^{o}C
Sample 2-6 tempered 1 h in order to simulate stress reliving of springs

Sample	Condition	UTS Mpa	Rp0,2 Mpa	A_{50} %	~Z %	no. of tests
1	as delivered	642	618	3	44	1
2	Stress rel a	641,5	620	2,75	44	2
3	Stress rel b	639	626	3,25	51,5	2
4	Stress rel c	643,3	604,0	2,0	45,3	3
5	Stress rel d	635,0	607,3	1,5	50,0	3
6	Stress rel e	624,7	588,3	2,8	48,0	3

From the results in the table above can be seen that stress reliving up to a certain temperature is possible without any effect on the material performance. If the material is aged or not by the supplier will probably influence the result. According to the test material supplier the UTS is 650 MPa which correspond well with the test results.



In the following table is given collected material performance data picked up from different companies and organisations data sheets. As can be seen the tested sample have slightly higher strength than presented in following table.

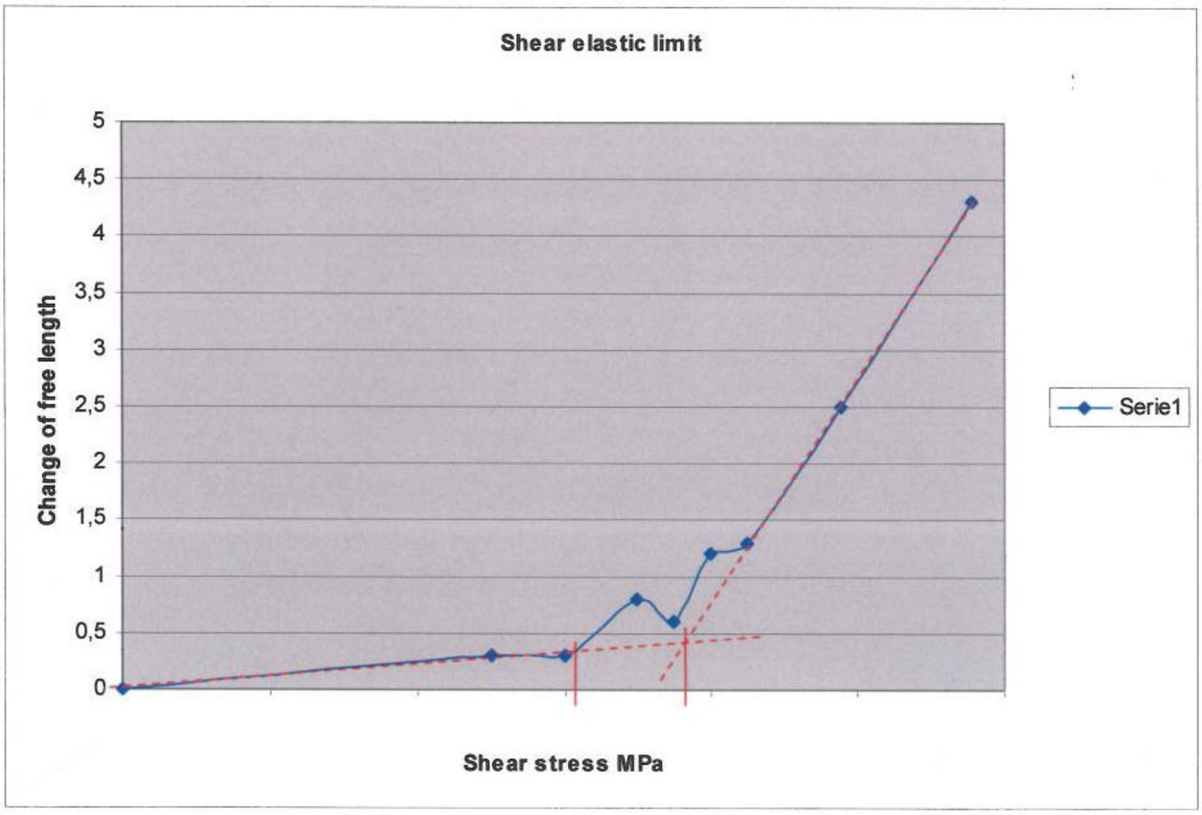
SA = solution anealed; SAH = solution anealed + age hardened; SAHC = solution anealed +age hardened + cold worked
SACH = solution anealed + cold worked +age hardened; SACP = solution anealed + cold worked + precipitation hardened

Company	UNS	Grades EN number	Condition	Rm Mpa	Rp0,2 Mpa	Elonga tion, A	Hardne HB	E-modul Mpa	G-module Mpa	Note
	--	CuZr, no.2.1580, CW120C								
CDA	C15000	---	H02	365	338/**	23	---	---	---	wire diam 12,7mm
CDA	C15000	---	O61	255	76/**	50	---	---	---	wire diam 6,35 mm
CDA	C15000	---	TF00	207	90/**	49	---	---	---	wire diam 2,29mm
CDA	C15000	---	TH04	524	496/**	1	---	---	---	wire diam 1mm
CDA	C15000	---	TH04	496	469/**	3	---	---	---	wire diam 2,29mm
CDA	C18150	---	TL02	469	400/**	19	---	---	---	wire diam 15,2 mm
CDA	C18150	---	TL02	469	338/**	15	---	---	---	wire diam 17,8 mm
CDA	C18150	---	TL04	469	455/**	15	---	---	---	wire diam 12,7 mm
CDA	C18150	---	TL04	469	434/**	20	---	---	---	wire diam 15,2 mm
Wieland	--	CuCr1Zr, no.2.1293, CW106C	s (=SA)	230	80	40	65	---	---	general data
Wieland	--	CuCr1Zr, no.2.1293, CW106C	a (=SAH)	460	340	20	130	---	---	general data
Wieland	--	CuCr1Zr, no.2.1293, CW106C	s (=SAHC)	470-570	420-540	15-10	140-170	---	---	general data
Thüssen/*	--	CuCr1Zr, no.2.1293, CW106C	SCAH	min.470	min.440	min. 8	160	108000		diam<25mm
Thüssen/*	--	CuCr1Zr, no.2.1293, CW106C	SCAH	min.440	min.350	min. 10	150	108000	45000	diam 25-50 mm
Thüssen/*	--	CuCrZr, CW106C	SCAH	min.540	min.450	min. 8	160	108000	45000	diam<20mm
Thüssen/*	--	CuZr, 1.1580, CW120C	SCAP	350	310	13	125	100000	---	diam <25mm
Thüssen/*	--	CuZr, 1.1580, CW120C	SCAP	300	250	20	105	---	---	diam >/=25mm
Luvata /*	C15000	---	SCAP	400-500	380-475	8-20	64-80	---	---	diam <25mm
Luvata /*	C15000	---	SCAP	350-420	320-400	10-20	64-69	---	---	diam 25-50 mm
Luvata /*	C15000	---	SCAP	~350	~330	10-20	~64	---	---	diam >50 mm
Luvata /*	C15000	---	SCAP	350-450	330-435	7-13	60-71	---	---	rolled
Cupralsa	C15000	---	SCAH	495	470	3		129000		wire diam 2,3 mm

note /* CDA = Copper Development Association; Thüssen = Thüssen Durometal Kronwestheim;
Luvata = Luvata Wolverhampton Ltd representing Outokumpu

The shear elastic limit of the material was tested on a not pre-stressed compression spring. The spring was compressed step by step and the change of free length for each step was measured. The shear stress for each step was calculated. Following diagram show the result. The small measured deformation in the beginning of the curve is caused by geometric deviations in the end coils. These end coils was also affected by the heat from the dry grinding. The result show that the shear elastic limit. The normal used value for metals 56 % of the UTS give 358 MPa and CDA says 2/3 x UTS which give 427 MPa, the indication is that 56 % is more correct. The stress values are not, bend radius, corrected values.

The coiled and stress relieved free length was made to give suitable pre-stressing rate (length loss in relation to the free length before pre-stress). The “synthetic” linear shear stress (MPa) at block length (no consideration to the elastic limit) was calculated at block length.
These pre-stress results give some lead in case of calculating for pre-setting. There was no problem with buckling or other undesirable deformations at used pre-stress levels.



Introduced residual stresses were estimated by using the shear elastic limit and the stress at block length on the finish springs (τ_{block} minus *shear elastic limit*). The average value for not corrected residual stresses was over 100 MPa (cross section average) and the average for corrected stresses was over 200 MPa (highest stressed fibre on the inside of the coils).

6/ Physical properties

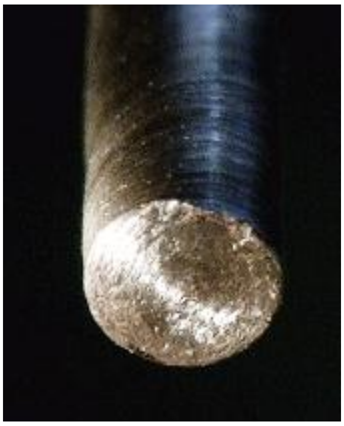
Company	UNS	Grades EN number	Density g/cm3	Termal expansion coeff. µm/m-^{o}C	Spec. heat Cap. j/kg ^{o}K
A	C15000	---	8,89	16,45 to 20,2	385
A	C18150	---	8,89	16,9-17,6	394
B	--	CuCr1Zr,	8,92	17,6	--
C	--	CuCr1Zr,	8,9	17	376
C	--	CuCrZr,	8,9	17	376
D	C15000	---	--		367

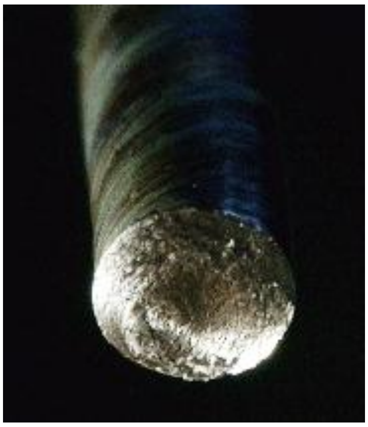
7/ Surface quality

The surface quality was tested on wire samples diameter 1,5 mm with help of torsion test there a length of 100 x diameter is twisted till breakage. At this test is a multi-axis stress state created with its maximum at the surface. A splitting fracture indicates defects at the surface or in the surface region of the wire. The higher the number of twists is the less is the brittleness of the wire. This test was made also on samples tempered for 1 hour at different degrees in order to simulate a stress reliving treatment.

Results:

Sample	Condition	number of torsions	type of fracture
1	as delivered	44	plane transverse clean shear fracture
2	temp. A	44	plane transverse clean shear fracture
3	temp. B	44	plane transverse clean shear fracture
4	temp. C	42	plane transverse clean shear fracture
5	temp. D	43	plane transverse clean shear fracture
6	temp. E	43	plane transverse clean shear fracture


Sample 1


Sample 6

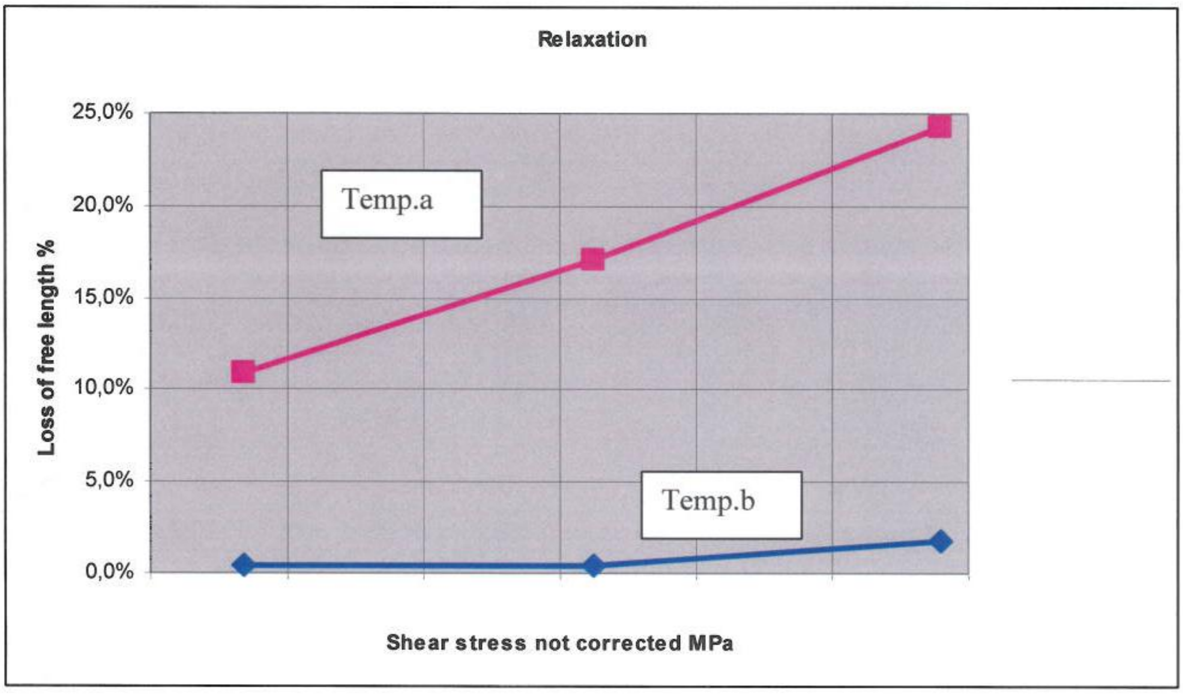

Sample 1


Sample 6

All samples have a plane transverse clean shear fracture and an equal pitch of the torsions along the length. No indication of surface defects is found. After treatment at some degrees the toughness looks to be some lower compared to other temperatures.

8/ Creep/Relaxation
No published data for this copper grade from material manufactures or other sources is found. Sample 1-6 was static loaded with the “bolt-method” and hold at two different temperatures. The springs were compressed to a specific length and hold at constant length at the temperature for 96 hours. Three different lengths giving three different stresses were used. The method used is a constant length method which means that developed relaxation lower the stress during the test hence the stress is not constant. The stresses were, as before, calculated with help of the deflection, no load measuring was made. Note that the springs are pre-stressed.

Following diagram give the relaxation result:



9/ Fatigue strength
No published fatigue data for springs made from this copper grade is found. Sample 7-10 was fatigue tested with different stress levels at room temperature. The machine used for the test have constant stroke and length set without load measuring or load control. This means that no compensation in case of relaxation/creep is made during the test. The stresses were, as before, calculated with help of the deflection, no load measuring was made. The tested springs were pre-stressed and the tests stopped after $1x10^6$ cycles. The springs showed good fatigue strength.
The length of the spring was measured before and after the test and there was no relaxation during the fatigue test.

10/ Plating
One manufacturer reports that the grades alloyed with Zr have good electroplating properties. This means that silver plating should work well. Electrolytic polishing is not recommended.

11/ Joining
Regarding welding there are some contradictory information for CuZr. For the CuZr alloy says one manufacturer that "zirconium copper can also be easily welded and it is well suited for electron beam welding". But there are other recommendations:

Joining Technique	Suitability
Soldering	Excellent
Brazing	Good
Oxyacetylene Welding	Not Recommended
Gas Shielded Arc Welding	Not Recommended
Coated Metal Arc Welding	Not Recommended
Spot Weld	Not Recommended
Seam Weld	Not Recommended
Butt Weld	Good

One other manufacturer give following information regarding joining of CuCr1Zr alloy.
Resistance welding - fair
Inert gas shielded arc welding - fair
Hard soldering - fair
Soft soldering - good

Lasers can be used for cutting and welding in a similar manner to electron beams but in air and not in vacuum. But lasers can give reflectivity problems which should be noted.
Electron beams are well suited to welding and useful in high conductivity metals such as copper. Normally this welding is carried out in a vacuum.
The high conductivity work-hardening alloys, whose strength depends upon previous cold working, suffer a serious and irreversible loss of mechanical properties when welded.
General about copper welding is that the oxide layer normally needs to be removed before welding.

12/ Other high conductivity grades
In following table are listed examples of copper alloys with high conductivity and reasonable strength.

Info source	grade	Type	UTS	% IACS
CDA	C18200	CuCr	460-593	80
Wieland K88	C18080	CuCrAgFeTiSi	400-650	75-85
Wieland K75	C18070	CuCrSiTi	550-630	78
Diehl Metal	?	CuMg0,4	560-740	62

forms and availability not investigated MPa

13/ Discussion
The sample tests are made with certified equipments, tolerances is maximum +/- 2 %. The coil springs was manually manufactured and this lead to a spread of length and number of active coils. Each spring was measured and the compression for relaxation and fatigue tests was adjusted according to calculated real stresses. No load testing was made, the stresses were calculated out from the dimensions and the compression for each individual spring. The length and spring diameter measuring was made with calliper. The limited number of tests samples lowers the statistical probability that the result average values are absolutely correct. The results should be used as performance indications. The data picked up from the material manufacturers is normally reliable. For latest up date of material data contact the actual material supplier.

14/ Conclusions
The copper grades alloyed with Zr and hardened by cold deformation and precipitation hardening show UTS up to about 650 MPa. The grade CuCr1Zr have better strength than grade CuZr and are probably better suited for springs. Coil springs can easily be manufactured from the CuCr1Zr alloy. Copper alloyed with zirconium is not toxic so no extra protection activities are needed during production.
The conductivity is 90 %IACS or higher for the CuZr alloy and 75 or higher for the CuCr1Zr alloy. The test made of CuCr1Zr wire gave 83 %IACS so this alloy have very high conductivity. Relaxation is higher than expected at higher temperatures. Fatigue strength is good here should be noted that the springs are pre-stressed before fatigue test. Plating of these grades is reported to work well. Joining by welding will lower the strength in HAZ (heat affected zone). This is because loss of part of the hardened effect from the cold deformation and the precipitation hardening. It is also reported that laser welding normally is not used for copper alloys because copper have high light reflection. The grade CuCr1Zr (UNS C18150) in solution annealed, cold deformation and precipitation hardened condition is suitable for different types of springs with high conductivity demands.

15/ Acknowledgements
Henrik Berner Lesjöfors sales handled the customer and supplier communication. Harald Pihl AB supplied the wire sample. Stece Fjäder AB coiled the compression springs. Springwire AB made the torsion tests. Exova AB Karlskoga made the tensile strength tests. Lesjöfors Industrifjädrar AB made the fatigue testing.

16/ References
Data sheets from: Wieland, Thyssen, Copper Development Association, Outokumpu and Cupralsa.

Metallverken, koppardata.
Zirconium Copper - a New Material for Use at Low Temperatures? Adam L. Woodcraft