解　　説

Ni-Ti 合金の形状記憶効果と超弾性

Shape Memory and Super-elasticity Effects in NiTi Alloys

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Summary: The equiatomic or near equiatomic NiTi is a unique intermetallic compound. It has good ductility, a shape memory effect, and a super-elasticity. The alloy undergoes a martensitic transformation at near room temperature. The low temperature phase is characterized by high damping capacity, and the high temperature phase by excellent abrasion and corrosion resistance. By a shape memory effect we mean that the alloy plastically deformed in the low temperature phase recovers its original shape in subsequent heating. Super-elasticity is a rubber-like behavior of the alloy in which a strain attained beyond the elastic limit in loading recovers upon unloading. The following is a presentation of the general properties and deformation mechanisms of the shape memory effect and the super-elasticity of the NiTi alloys including its applications such as in jointing devices, thermal actuators, and medical devices.

1.　多様な特性を持つ Ni-Ti 合金

ニッケルとチタンを原子比１：１で含む Ni-Ti 合金は，金属間化合物であるのに塑性加工が可能というめずらしい性質を持っているが，さらに，室温付近の特定の温度でマルテンサイト変態し，これに伴って特異かつ多様な挙動を示す合金である。

まず，この合金はマルテンサイト変態温度（以下，M変態温度と略記する。M変態については後段の形状記憶効果のメカニズムの項で説明するが，ここではある特定の温度という位に解釈しておいていただきたい）以下の温度で，非常に大きな振動減衰能を有することが知られている[1)]。もともと，この合金が米海軍の研究所（Naval Ordnance Laboratory）で開発されたきっかけが，潜水艦のソナー対策用防音材であった位であるから，第一の特徴と言って良いであろう。この特性は，当然，制振材や防音材として実用が考えられている[2)]。

合金の第二の性質は，M変態温度近くの温度領域，正確にはM変態温度をまたいで，M変態—M逆変態のサイクルを行ったとき現れる形状記憶効果である。これは，M変態温度より低い温度で変形した後，M変態温度以上に加熱すると，変形前のもとの形に戻る現象である[3)-5)]。

M変態温度より少し高い領域では，合金の第三の性質である超弾性現象が見られる。これは降伏点をはるかにこえる数パーセントもの変形ひずみが，除荷するだけでゴムのようにもとに戻ってしまう現象で，擬弾性，ゴム弾性と呼ばれることもある[6)]。

M変態温度よりずっと高い温度領域では，これまでのような変った現象は見られないが，すぐれた耐食性と耐摩耗性を兼ね備えた構造材として大変好ましい性質となる。この第四の特性は化学プラントをはじめとする耐食摺動部にすでに実用されている。

以上，ごく簡単に述べた特性のうち，第四の耐食，耐摩耗性については本誌に発表しているので[7)]，本稿では

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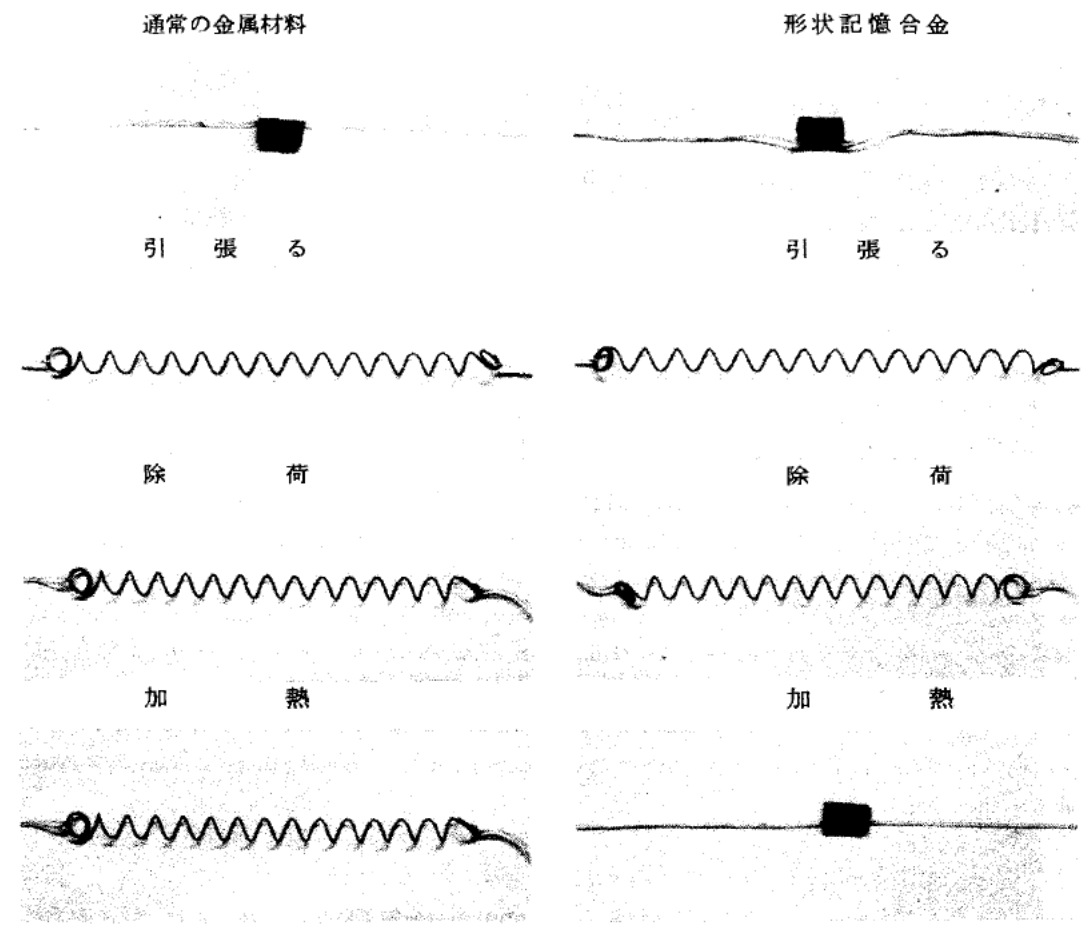
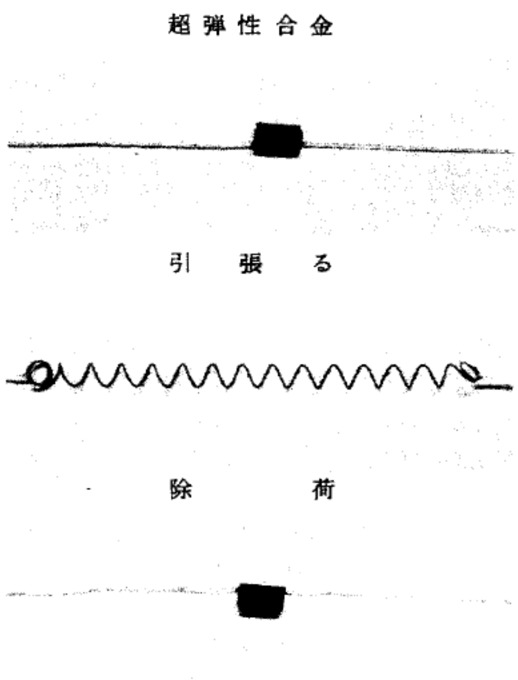
Exhibit 1012-0001

写真1　形状記憶合金と超弾性合金





最近機能材料としてとみに注目されている形状記憶効果と超弾性について実用例を紹介しながら解説する。

2. 形状記憶効果と超弾性

形状記憶効果，超弾性現象はすでに述べたように，降伏点をこえる変形ひずみが，それぞれ加熱したり除荷するだけでもとに戻る現象であるが，これを実物の写真1と応力・ひずみ線図（図1）を使ってもう少し具体的に説明しよう。

通常の金属材料では，弾性限以下の変形ひずみは除荷時に完全にもとに戻るが，ひずみが弾性限をこえ降伏領域に入ると，変形応力を除いたとき，弾性変形分しかひずみが回復せず，塑性変形分が残留して永久変形となる。

形状記憶効果を示す合金，つまり，形状記憶合金に変形応力を加えると，弾性変形による直線領域に続いて，やはり降伏が見られ，除荷後は見かけ上の塑性変形が残る。この変形は，通常の金属材料で見られる転位すべり

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によるものではなく一種の双晶変形であるが，見掛けはすべりによる塑性変形とかわるところはない。しかし，これらの変形ひずみは合金をM変態温度以上に加熱すると，変形前のひずみゼロの状態に戻ってしまうのである。

一方，超弾性の場合はひずみの回復に加熱を必要としない。降伏領域まで変形した後，除荷すると，図1に示すように，ちょうど降伏現象と逆の挙動を示しながらひずみゼロに戻るのである。

ここで注意すべきことは，形状記憶効果や超弾性によって回復できるひずみ量には一定の限度があり，変形のし方によってはもとに戻らなくなることである。この点について，高ひずみ領域の応力・ひずみ線図（図2）を使って説明する[8]。

M変態温度以下の温度で形状記憶合金を変形すると，弾性変形①に続いて降伏がおこり，応力はほぼ一定の値をとる。平担部②の途中から除荷すると，見掛けの塑性ひずみ③が残るが，これはすでに述べたように加熱すると消失する。ところが，変形ひずみが増して，平担部をこえると，応力は再び増加をはじめ，加工硬化がはじまる。ある程度加工硬化した状態④から除荷すると，やはりひずみ⑤が残留するが，これをM変態温度以上に加熱してもひずみは完全には回復しないで永久変形となる⑥。さらに変形ひずみが増すと，応力の増加はゆるやかになり最後は破断する。充分に加工硬化した状態⑦では加熱しても殆ど形状を回復しない。

したがって，良好な形状回復特性を得るには，変形ひずみの量が一定の値(Ni-Ti 合金では7.5%) をこえないようにする必要がある。これらの事情は超弾性についてもまったく同じである。

形状記憶効果と超弾性は，いずれも1950年代の前半に金とカドミウムの合金で偶然に発見された現象であるが[9]，当時は特殊な合金系であることなどからあまり注目されなかった。形状記憶効果がさかんに研究されるようになったのは，NOL (前述) で Ni-Ti 合金の顕著な形状記憶効果が発見されてからのことである[10]。以来，多くの研究成果が発表され，形状記憶効果を示す合金もこれまでに十数種類が見つかっている。

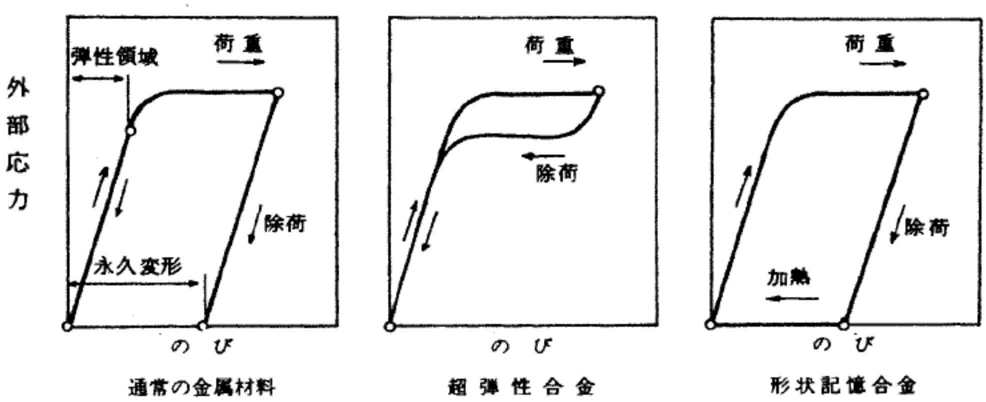

図1　形状記憶合金，超弾性合金と通常の金属材料の応力ひずみ線図

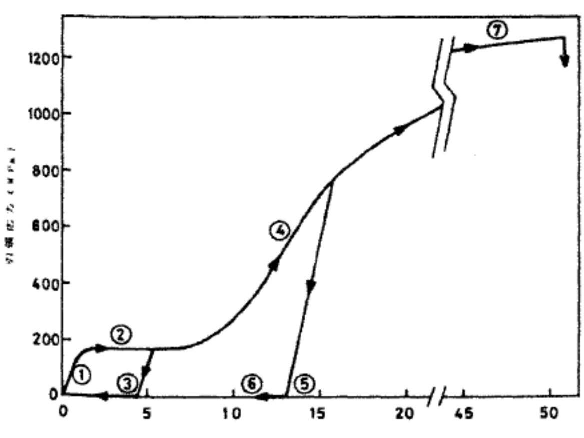

図2　形状記憶 NiTi 合金の応力ひずみ線図

ところが，Ni-Ti 合金の発見当時はこの合金が超弾性を持つことは判っておらず，超弾性は形状記憶効果とは別個の現象として Cu-Al-Ni合金などを中心に研究がなされていた。Ni-Ti 合金の超弾性現象が見つけられたのは，1970年代に入って両者の現象がいずれも熱弾性型M変態によって起ることが解明される直前のことである[11][12]。

一方，高温相の耐食，耐摩耗性は形状記憶効果などの機能材としての興味とはまったく独立に，構造材として開発がすすめられ，機能材としてよりずっと早い時期に実用化され，現在に至っている。

3. 形状記憶効果と超弾性のメカニズム

形状記憶効果や超弾性が何故起るかというと，これが

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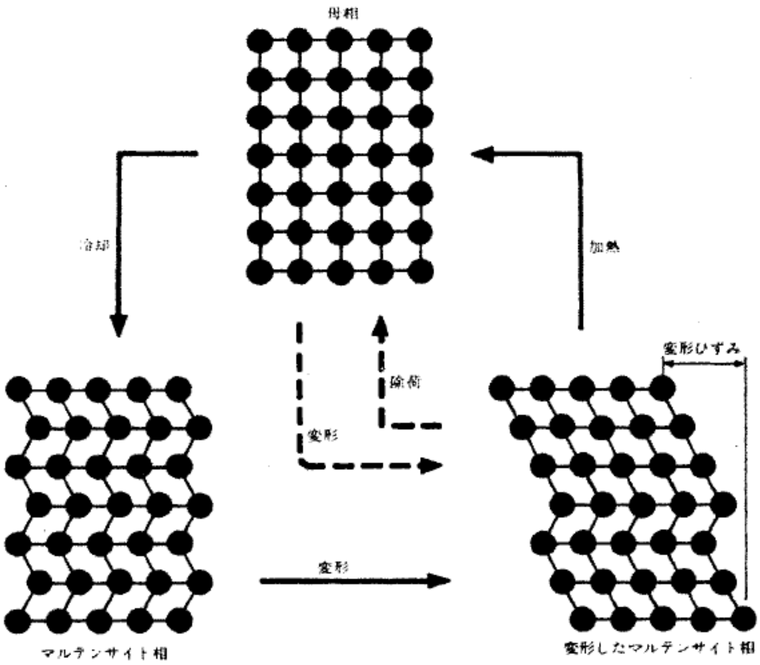

図 3　形状記憶効果と超弾性のメカニズム（模式図）

仲々複雑で，また，学問的に不明な点も少くない。ここでは，これまで判っている範囲でそのメカニズムを単純化して説明するにとどめる（図 3 参照）。

形状記憶合金を高温のオーステナイト相（以下，A相と略記する）から冷却してある特定の温度（M変態開始温度。Ms 点と呼ばれる）を通過させるとM変態してA相からM相になる。M変態は，鉄鋼を急冷した際に起る変態として有名であるが，チタンやジルコニウムその他の金属，合金でも見られる現象で，固相のまま拡散を伴わずに主にせん断変形によって結晶構造がかわる相変態の一種である[13]。このM相を加熱してM相がA相に逆変態する温度（冷却時の Ms 点より若干高温側にあり，Af 点と呼ばれる。先に述べたM変態温度はこの Af 点のことである）以上にすると再びA相に戻るが，外力が加わらない時にはこの変態・逆変態のサイクルによって合金のマクロな形状が変化することはない。ところが，M相に変形応力が加わると事情が異ってくる。この場合，応力が降伏応力をこえると前述のごとく，見掛け上の塑性変形をするが，これは結晶がその向き（方位）をかえて変形をまかなう一種の双晶変形である。このため，結晶のならび方を組換えて進行する転位すべりによる変形と違って，変形の前後で結晶間のつながり方が同じ関係に保たれる。このように変形したM相を加熱するとA相に逆変態するが，結晶間のつながり方を保ってA相に戻るため，結晶全体ももとの形に戻るのである。

一方，超弾性もやはりM変態に伴う現象であるが，形状記憶効果におけるM変態が熱つまり温度変化によって引起されるのに対して，超弾性では応力によって引起される点で異なる。この型のM変態は応力誘起変態と呼ばれ，Af 点より若干高い温度でA相に応力を加えたとき応力，主にせん断応力が駆動力となってM相に変態するものである。その際，同じ応力によってM相の変形が行われるため，図 4 の破線で示すようにA相から一挙に変形M相に移行する。これを除荷つまり応力を除くと，もともとその温度（Af 点以上）で安定なA相に戻ることになるが，ここでも結晶間のつながり方を保ったまま元のA相に戻るため変形ひずみが解消するのである。

ところで，M 変態は Ni-Ti のような特殊な合金にだけ見られる現象ではない。鉄鋼をはじめ，多くの金属，合金で見られるポピュラーな現象である。しかし，鋼は最も典型的なM変態をする合金であるが，形状記憶効果や超弾性を示さない。一部の Ti 合金や Co 合金はある程度のひずみ回復を示すが，不完全である。これらの違いの原因は変態の際のA相とM相の界面の整合性にあると考えられている。整合性の良い Ni-Ti 合金などにおけるM変態（熱弾性型M変態と呼ばれる）の場合はM相がA相に戻るとき，原子がそれぞれもとの配列に戻るので形状を回復するが，鉄鋼などのM変態の場合は必ずしももとの位置に戻らず，エネルギー的に有利な適当な配列のA相に戻る。したがって，多少形状が回復することはあっても，完全に変形前の形状に戻ることはない。これら界面の整合性に加えて，規則格子の形成によってM相の兄弟相（結晶の形が同じで方位だけが異なる相）の数が制限されることも原子がもとの位置に戻るための重要な要因となっている。これらの要件のすべてが満たされたときにはじめて良好な形状記憶特性や超弾性特性が得られるのである。

4.　形状記憶 Ni-Ti 合金の応用

形状記憶 Ni-Ti合金の実用化第一号はパイプ継手[14]である。継手には動作温が低い（−150℃位）合金を用い，内径をパイプ外径よりやや小さく作っておく。接続作業はまず継手を液体空気に侵け，内側にプラグを押込んで内径を拡げてやる。次に，図 4 のように両側からパイプ

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Exhibit 1012-0004

を挿入し，室温に放置すると，継手の径が拡管前の寸法に戻り，パイプを締め付けるわけである。この継手はジェット戦闘機F—14の油圧配管系にすでに10万個以上も使われており，油漏れその他のトラブルのまったくないことが確認されている。パイプ継手と似た使い方として，各種のシーリング，クランプなどがある（図5，図6）。

Ni-Ti合金は生体への適合性が良いので，生体に埋込んで使用するインプラント材として期待されている。折れた骨をギプスによらずボルトなどで生体で固定する内固定接骨法に使用する接骨板は広く研究されているものの一つである。同じ様な用途に髄内釘や人工関節基部の固定法がある。彎曲した脊柱に直線状を記憶したNi-Ti合金を沿わせて固定し，外部から加熱し脊柱を真すぐにする側彎症の治療法は形状記憶合金ならではの方法である。

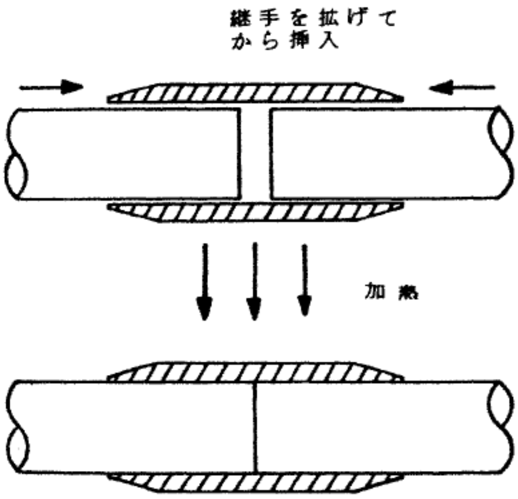

図4　形状記憶 NiTi 合金を用いたパイプ継手の原理図

図5　形状記憶合金を用いたIC素子パッケージのシーリング

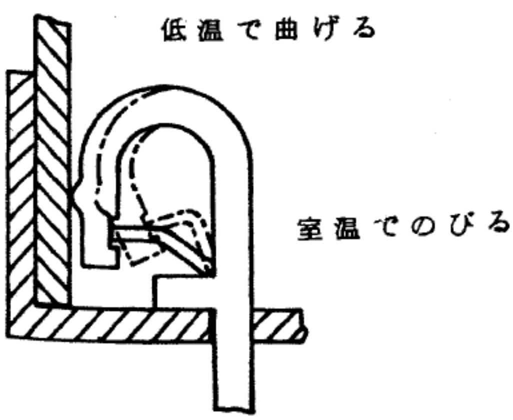

図6　形状記憶 NiTi 合金製クランプ

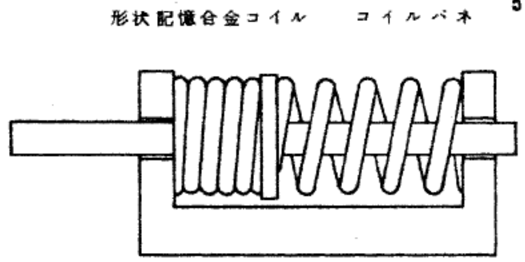

図7　バイアスバネによる二方向性形状記憶素子の動作原理図

さて，これまで述べてきた形状記憶効果はいずれも一方向性(One way)と呼ばれる現象である。つまり，合金を低温で変形した後に加熱すると一回だけ元に戻る現象で，これを再び低温にしても低温で変形した時の形にはならない。しかし，能動素子は一般的に一方向性より繰返し動作をする二方向性(Two way)の素子の方が機能的に有用であり，応用範囲も広い。このため，形状記憶合金についても二方向性特性を得る方法がいろいろと考えられているが，その一つにバイアス力を用いた方法がある。これは形状記憶合金が高温で強く（硬く，降伏応力が高い），低温で弱い（軟かく，降伏応力が低い）という性質を利用したもので，例えば図7のような，形状記憶合金のコイルと通常のコイルバネを互に押合うようにした素子の場合，低温では形状記憶合金がバネの力に負けて左側に押付けられているが，温度が上がるとバネの力に打勝って右側へ動くわけである。

二方向性素子としては，この他に差動式二方向性素子が良く使われる。これは高温と低温における形状記憶合金の力の差を取出すもので，例えば図7のコイルを両方共形状記憶合金で作るとこのタイプの素子になる。一方のコイルを加熱すると温度の上ったコイルが反対側のコイルを押込んで力を発生する。コイルの加熱を止めて反対側のコイルを加熱すれば逆方向へ動くのである。

二方向性の温度検出素子としては，昔からバイメタルが良く知られているが，形状記憶素子は発生する力が大きいこと，形状変化が特定の温度で急に起こり変化量が桁違いに大きい点でバイメタルよりすぐれている。特に発生力の大きなことは，温度検出部（センサー）と駆動部（アクチュエーター）を一つの素子で兼ねることを可能にし，この素子の最大の利点となっている。ただ，駆動源が熱であるため大きな出力を出そうとして寸法の大

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Exhibit 1012-0005

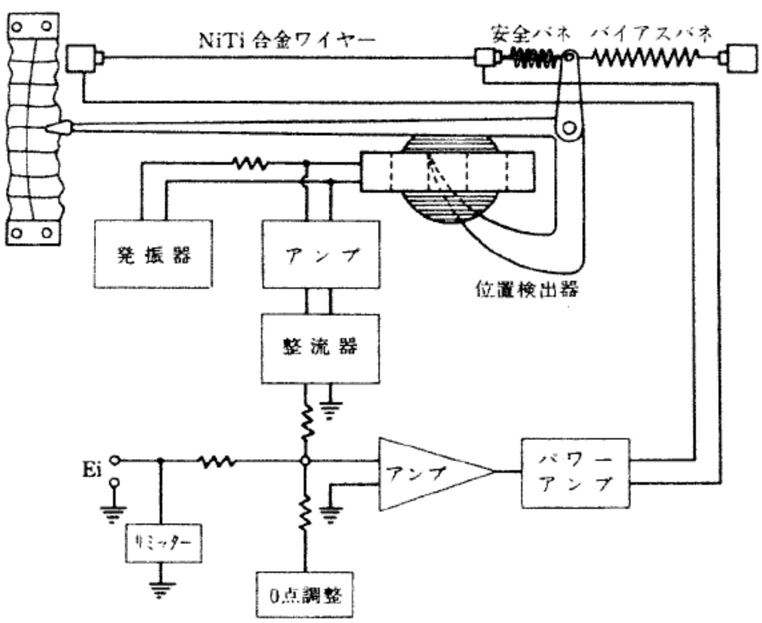

図 8 形状記憶素子を用いたペンレコーダー駆動部の構成図

きな素子を使用すると動作速度がどうしても遅くなるという点は注意すべきである。

Ni-Ti 合金は耐食性が良いのでこれを用いた素子は温度以外の環境や雰囲気に非常に強い。さらに，モーターなどと違って可動軸封部（シール）を必要としないので，環境条件の厳しい場所や外界と隔離された場所での使用に適しており，実際に，高真空や原子炉内での応用が検討されている[15]。

二方向性素子の応用例として，ペンレコーダーの駆動装置がある。これは図 8 に示す構造をしており，バイアスバネで引張られた直線状の Ni-Ti合金ワイヤーに通電加熱して動作させる。ペンの位置はフィードバックされヒステリシスや温度変化による誤差を生じないように設計されている。

図 9 はコネクター[16]であるが，前述のパイプ継手と違って二方向性動作をし，何度でも繰返し使用できる。内側のベリリウム銅製のスリーブには割りが入っていて，フリーな状態では先端が開いている。スリーブの外側には，動作温度が室温より低い Ni-Ti合金のリングがはめられ，低温ではスリーブのバネ力によって口を開いているが，室温ではリングが形状回復して相手導体を締めるのである。冷却はスプレーで冷却ガスを吹付ける方法が一般的である。二方向性素子としては，この他に各種の温度スイッチ，サーキットブレーカー，火災安全装置が発表されている。

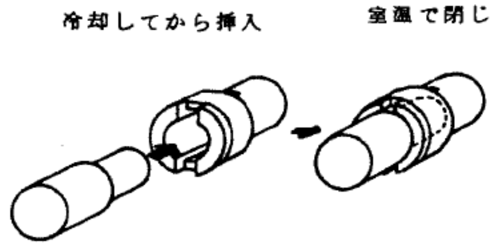

図 9 形状記憶合金を用いたコネクター

自動車関係での開発もかなりさかんで，ラジエーターサーモスタットとファンクラッチがその内でも特に有望である。前者はエンジン冷却水の温度が上昇した時だけラジエーターに導いて冷却水の冷却を行うものであり，後者はエンジンが一定温度に暖まった時，冷却ファンを回転軸につないで冷却をする仕組である。いずれも暖気時間の短縮と省エネルギーを目的としたものであるが，温度変化によるガソリン粘度の違いを形状記憶素子で補正し，常に最適の混合比を得る気化器の噴射ノズルなども考案されている。

差動式形状記憶素子は発生力が大きく，エネルギー変換効率が高いので，ロボットをはじめとする各種のアクチュエーターやマニピュレーターに応用されるだけでなく，排熱などの低品位エネルギーから機械エネルギーを取出す熱エンジンへの応用が期待されている(図10)。これらの熱エンジンはまだ実用化されてはいないが，研究開発はかなり活発で，1978年に米国でヒートエンジンのコンファレンス[17]が開催されたほどである。

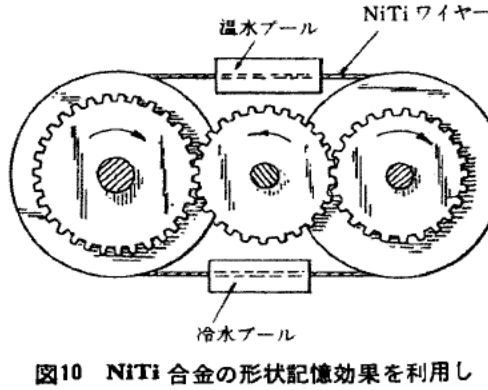

図10 NiTi 合金の形状記憶効果を利用した熱エンジンの例

5. 超弾性 Ni-Ti 合金の応用

超弾性の実用化第一号は，眼鏡のフレームである[18]。

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Exhibit 1012-0006

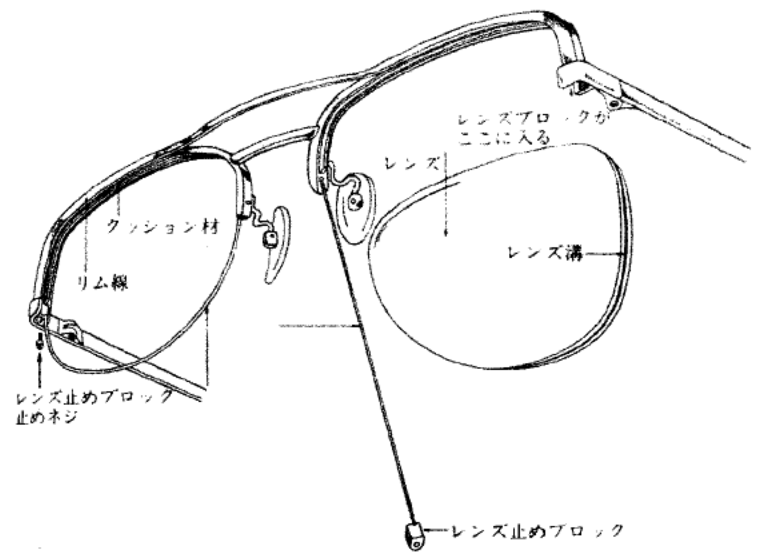
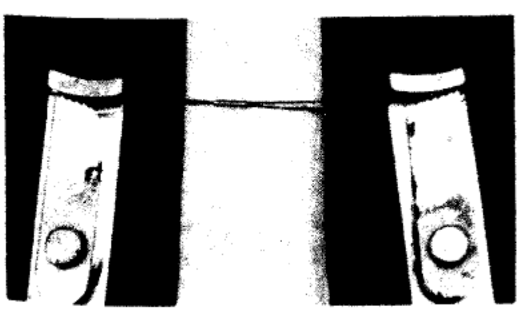


図11　超弾性 NiTi のワイヤーを使った眼鏡フレーム

Ni-Ti合金は図11に示すようにレンズを固定するワイヤとして使われている。従来，このように金属や合成樹脂のワイヤでレンズを吊って固定する方式のフレームは，軽くて視野が広いという利点の反面，レンズを拭いたとき，寒さでレンズが収縮したときに外れるなどの問題があり，充分に機能したフレームを作ることができなかった。開発されたフレームでは，レンズを強く拭いたり，温度が変化しても超弾性ワイヤが追従して保持することによりこれまでの欠点をすべて解決している。

超弾性 Ni-Ti合金は形状記憶材と同じように医療関係に応用されている。その一つは咬合の改善，いわゆる歯の矯正に関するものである。不正咬合をワイヤの弾性によって矯正するフルバンドシステムはすぐれた方法であるが，通常の金属ワイヤ（ステンレス鋼，Co-Cr合金など）では弾性範囲がせまいため治療の進行に従って何度もワイヤを交換しなければならなかった。また，弾性範囲を拡げるためにループを作ったりすると装着中の不快感が増す欠点もあった。超弾性ワイヤを使用すればこれらの問題を解決でき，さらに応力・ひずみ線図から予想されるように，矯正が進行しても矯正力が低下しないという大きなメリットが生ずる。このため，ワイヤ特性の改善の他，ワイヤと骨の固定，最適アーチ形状など，その特性を生かすための総合的な研究が進められている[19]。Ni-Ti 合金ワイヤは米国ではすでに半分近くの矯正医に使用されているが，これは Ni-Ti合金のM相を加工硬化して弾性範囲を拡げたもので本来の超弾性とは若干その特性や使い方が異なる。

写真2　超弾性 NiTi 合金線による骨の結束



整形外科関係では，骨の結束法に応用例がある[20]。一般に生体組織は外部からの負荷を自動的に緩和する作用があり，骨の場合もステンレス線などで強く結束すると骨組織が緩和作用で溶け出し，結束状態を長期間維持することができない。これが超弾性ワイヤだと，骨が溶け出しても超弾性の範囲内の縮みであれば追従し，治療期間中良好な結束が保てるのである。ところが，超弾性ワイヤにも問題がないわけではなく，例えば通常のワイヤのようにペンチでよじって締め付けようとしても元に戻って固定することができない。この問題は細いパイプにワイヤを通してからカシめて固定すをことで解決した(写真2)。この結束法はすでに臨床で使われている。

超弾性合金は通常のバネ材より一桁以上も大きなひずみ回復能力があるので，当然，汎用のバネ材として期待されている。また，超弾性バネは本質的に非線型バネなので，非線型性をうまく利用すれば機能性バネとして大変有効である。その反面，弾性ひずみでないため剛性率やバネ定数から荷重と変位の関係を求めることが難かしいとか，ひずみ量が大きく，ねじりモーメントでコイルバネのひずみ状態を近似することに無理があるといったバネの設計上の難しさがある。このため，加工法，熱処理法などのハード技術と並行して，バネ設計法を中心としたソフト面の開発が進められている。

超弾性合金には，ひずみ回復能に加えて，応力・ひずみ曲線上のヒステリシス特性からくる大きな振動減衰能があるため，その特性を積極的に利用すること，例えばチャタリング防止機能を持つ接点バネに使用することが，精密機械関係の分野で検討されている。

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Exhibit 1012-0007

6. おわりに

以上述べたように，Ni-Ti 合金の形状記憶効果と超弾性は一部は実用化されているとはいうものの，まだ開発段階にあり，ハード面ソフト面いずれも技術的に完成されたものとは言い難い。しかし，数パーセントにおよぶ変形ひずみが回復するユニークな性質は，機能材料としてきわめて好ましいものであり，多くの分野で広範な応用が期待されている。

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Exhibit 1012-0008

Shape Memory and Super-elasticity Effects in NiTi Alloys

Yuichi Suzuki

Summary: The equiatomic or near equiatomic NiTi is a unique intermetallic compound. It has good ductility, a shape memory effect, and a super-elasticity. The alloy undergoes a martensitic transformation at near room temperature. The low temperature phase is characterized by high damping capacity, and the high temperature phase by excellent abrasion and corrosion resistance. By a shape memory effect we mean that the alloy plastically deforms in the low temperature phase and recovers its original shape in subsequent heating. Super-elasticity is a rubber-like behavior of the alloy in which a strain loading beyond the elastic limit recovers upon unloading. The following is a presentation of the general properties and transformation mechanisms of the shape memory effect and the super-elasticity of the NiTi alloys including its application such as in jointing devices, thermal actuators, and medical devices.

1. Ni-Ti alloys have various characteristics

A Ni-Ti alloy containing nickel and titanium in the atomic ratio of 1:1 shows unique characteristics. Although it is an intermetallic compound, it can be worked plastically. Furthermore, the alloy undergoes a martensitic transformation at a certain temperature near room temperature. The alloy shows various unique forms of behavior in accordance with the martensitic transformation.

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It has been known that this alloy has a great damping capacity at temperatures below martensitic transformation temperature (abbreviated to M-transformation temperature hereinafter; this M-transformation will be described in the section on mechanisms below, but it is to be understood here to be a certain temperature or the like.[1] The alloy was developed by the Naval Ordnance Laboratory (NOL) as a soundproofing material for submarines as a countermeasure against SONAR. The damping capacity can be called the first feature. The damping characteristic could therefore conceivably be used as a damping material or a soundproofing material.[2]

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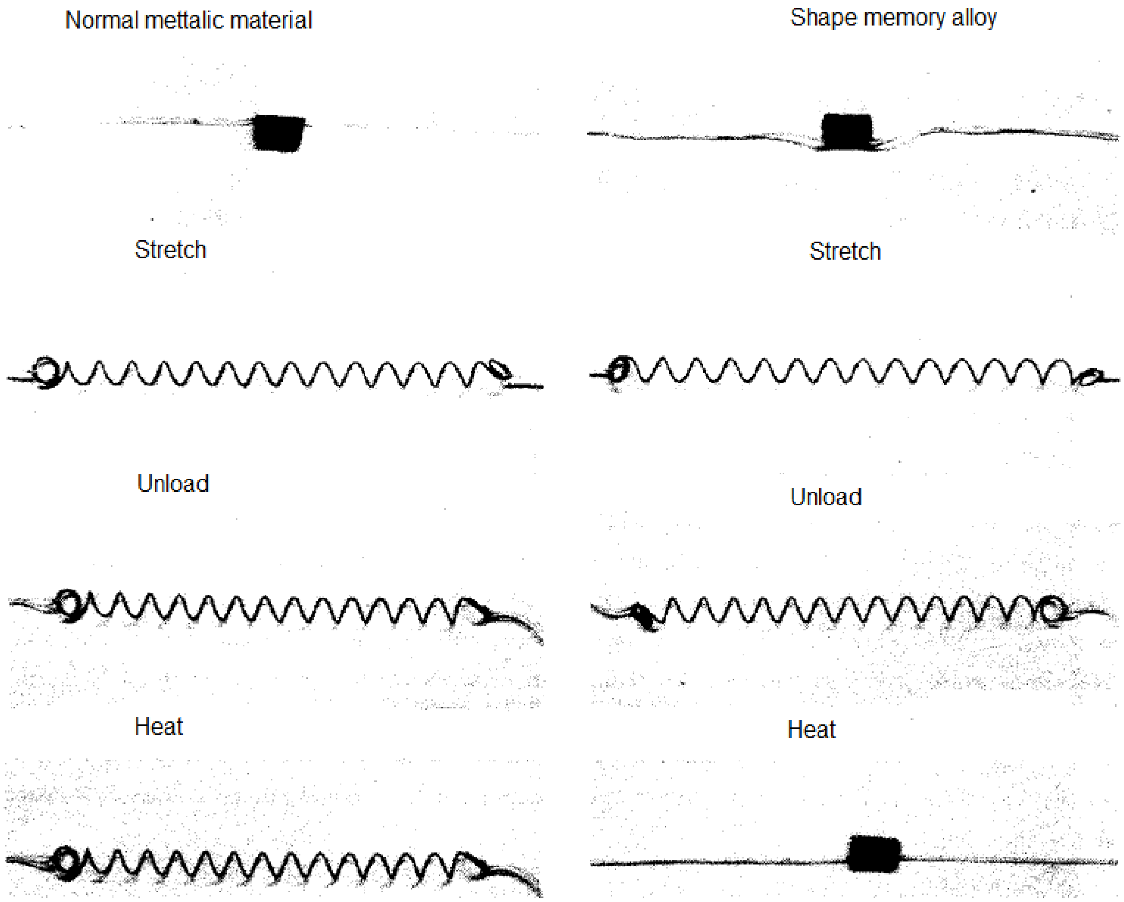
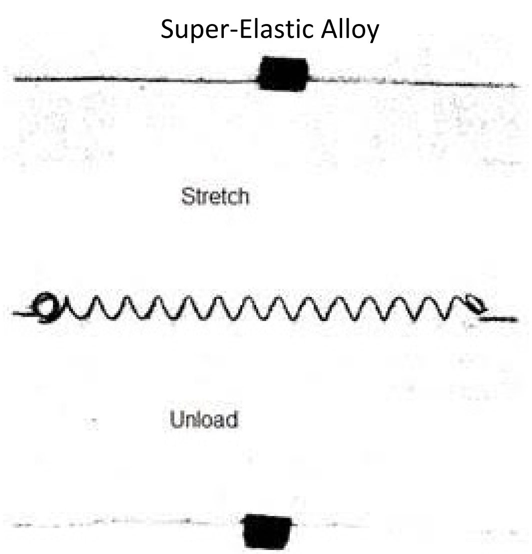
Photograph 1 Shape memory alloy and super-elastic alloy





The second feature of the alloy is characterized by a shape memory effect which appears when the M-transformation and a reverse M-transformation are cycled in a temperature domain near the M-transformation temperature, precisely speaking, one that straddles the M-transformation temperature. This phenomenon is characterized in that when the alloy is heated to a temperature higher than the M-transformation temperature after it has been deformed at a temperature lower than the M-transformation temperature, its shape recovers to its original form.[3) - 5)]

The third feature of the alloy, super-elasticity appears in a temperature domain slightly higher than the M-transformation temperature. This is a rubber-like behavior in which a deformation strain of several percent which significantly exceeds the yield point is recovered only upon unloading, so this behavior is sometimes called false elasticity or rubber elasticity.[6)]

Although these unique phenomena do not appear in a temperature region much higher than the M-transformation temperature, these characteristics of the alloy become significantly advantageous in a structured material having both excellent corrosion and abrasion resistances. The fourth feature has been previously made use of in certain portions of chemical plants or the like where rubbing takes place and where corrosion resistance is required.

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Exhibit 1012-0010

Since the fourth feature consisting of corrosion and abrasion resistances as described above has been previously disclosed in this magazine,[7] the shape memory effect and super-elasticity which have recently become of major interest for functional materials will now be described with introducing practical examples.

2. Shape memory effect and super-elasticity

As described above, the shape memory effect and super-elasticity are phenomena in which a deformation strain exceeding the yield point can be reversed only by heating or unloading. These phenomena will now be more specifically described with reference to actual photographs and stress-strain diagrams (Fig. 1).

On the other hand, a super-elastic alloy does not require heating for recovering from strain. If the load is removed after the alloy has been deformed to the yield region, the strain, as shown in Fig. 1, returns to zero, exhibiting a behavior which is the opposite of the yield phenomenon.

It must be noted here that the amount of strain which can be reversed by the shape memory effect or super-elasticity has a certain limitation. Strain sometimes cannot be recovered from, depending on the manner of deformation. The point will now be described with reference to a stress-strain diagram covering a high strain domain (Fig. 2).[8]

When a shape memory alloy is deformed at a temperature below

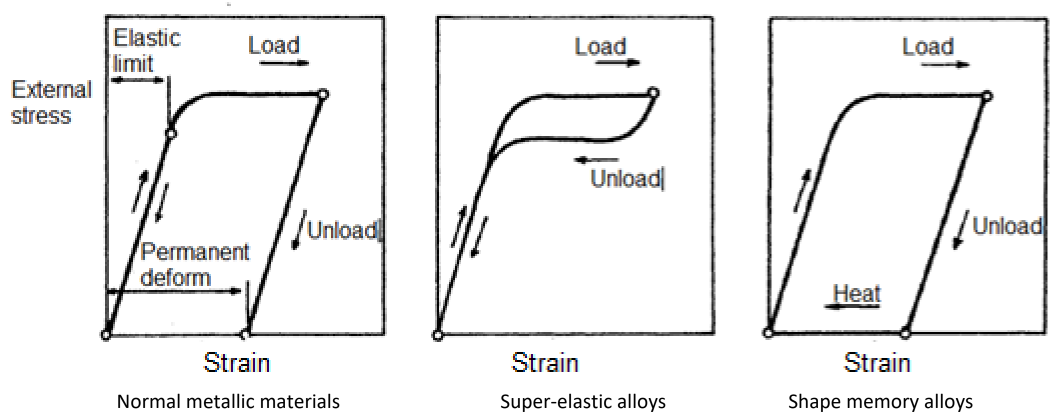

Fig. 1 Stress-strain diagrams of shape memory alloy, super-elastic alloy, and normal metallic material

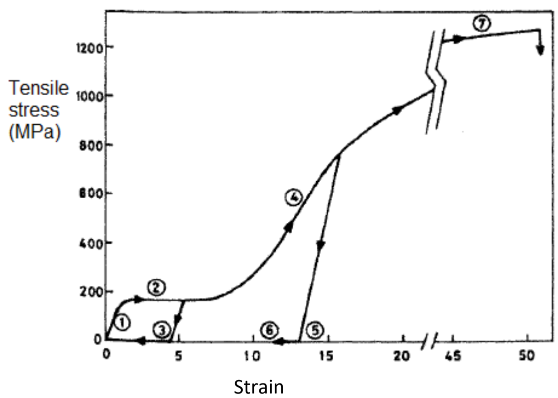

Fig. 2 Stress-strain diagram of shape memory Ni-Ti alloy

A normal metallic material completely recovers from a deformation strain below its elastic limit upon unloading, but if the strain enters the yield region after exceeding the elastic limit, only the elastic deformation can be reversed upon unloading, leaving plastic deformation which creates permanent deformation.

If deformation strain is applied to an alloy exhibiting the shape memory effect, that is, a shape memory alloy, yield is similarly seen after the straight-line region caused by elastic deformation, and apparent plastic deformation remains after unloading. This deformation does not depend on displacement slip which is seen in usual metallic materials, but it is a kind of hemitrope deformation, but the appearance bears no relation to the plastic deformation due to slip. However, these deformation strains can be cancelled and the original, strain-free, shape can be regained by heating the alloy to a temperature above the M-transformation temperature.

the M-transformation temperature, yield occurs after elastic deformation 1, and the stress becomes approximately constant. If the load is removed at an intermediate portion of the flat portion 2, apparent plastic strain 3 remains, but this strain is removed by heating, as mentioned above. However, if the deformation strain increases so as to exceed the flat portion, the stress again begins to increase, and work hardening begins. If the load is removed when the work hardening has progressed to a certain degree 4 the strain 5 also remains, but this strain cannot be recovered from by heating to a temperature beyond the M-transformation temperature, resulting in a permanent deformation 6. If the deformation strain further increases, the increase in stress becomes moderate, and finally the material breaks. A material which has been extensively work-hardened 7 will not recover its shape by heating.

Therefore, it is necessary to restrict the amount of strain to below a certain value (7.5% in Ni-Ti alloy) in order to obtain an excellent shape recovery characteristic. This is exactly the same as the condition for super-elasticity.

Both the shape memory effect and super-elasticity were accidently discovered in an alloy consisting of gold and cadmium in the early 1950s,[9] but they did not attract much attention at the time because of the rarity of the alloy. The shape memory effect was not studied much until after significant shape memory effects were discovered in Ni-Ti alloys by the NOL (as described above).[10] Since

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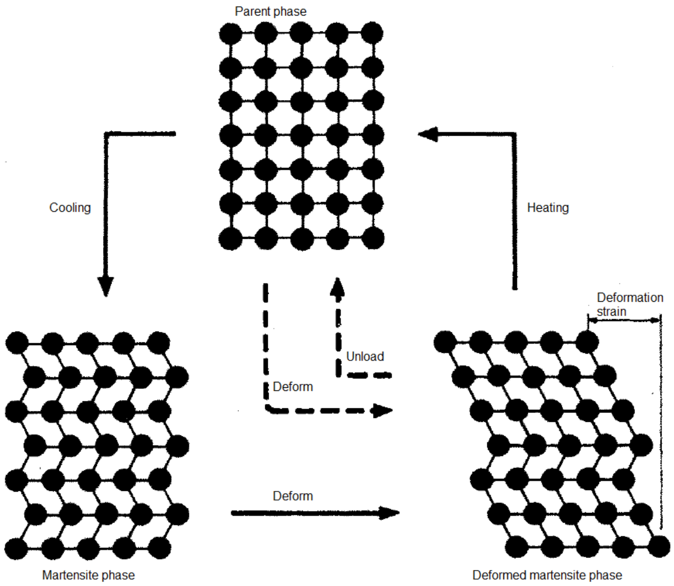

macrostructure of the alloys are not changed by this cycle consisting of transformation and inverse transformation. However, the case is different if an external force is applied to the M phase. In this case, if the stress exceeds the yield-stress, apparent plastic deformation occurs as mentioned above, but this deformation is a sort of hemitrope deformation in which the crystals change their direction (azimuth) to absorb the deformation. Therefore, in contrast to the deformation which is proceeded by displacement slip, in which the arrangement of the crystals is changed, the connections between the crystals are the same before and after the deformation. If the M phase which has been transformed as described above is heated, it transforms back to the A phase. However, since the connections between the crystals remain as the material returns to the A phase, the overall shape of the crystals recovers its original form.

Super-elasticity is also a phenomenon which depends upon M-transformation. However, the M-transformation which generates the shape memory effect is caused by heat, that is, a change in temperature, while the M-transformation which generates super-elasticity is caused by stress. The M-transformation of the type described above is called stress transformation, in which stress, mainly shear stress, acts to transform the A phase to the M phase when a stress is applied to the A phase at a temperature slightly higher than the Af point. In this case, since the stress also causes transformation to the M phase, the A phase suddenly shifts to a transformed M phase, as shown by the dashed line in Fig. 3. The removal of the load, that is, the removal of the stress, causes a return to the A phase which is originally stable at this temperature (above the Af point). This return to the A phase maintains the connections of the crystals, and so releases the strain.

M-transformation is not a phenomenon displayed only by special alloys such as Ni-Ti alloys. It is a phenomenon displayed by many types of metal such as steels and alloys. Although steel is an alloy which typically exhibits M-transformation, it does not display any shape memory effect or super-elasticity. Some Ti alloys and Co alloys exhibit stress recovery to a certain extent, but this is not complete. The reason for this difference is considered to depend on the consistency of the phase boundaries between the A phase and the M phase. In M-transformation (called thermal elastic M-transformation) in an extremely consistent Ni-Ti alloy, when the M phase returns to the A phase the atoms return to their original arrangement, so that the shape can be recovered. However, in M-transformation in steel or the like, the atoms do not necessarily return to their original positions; they return to a suitable sort of A phase in which they are arranged advantageously from the energy point of view. Therefore, the shape can be recovered to some extent, but it cannot be completely recovered. The fact that the number of hemitrope phases of the M phase (in which the shape of the crystals is the same, but only their azimuths differ) is limited by the way in which the super lattice is formed is an important factor, in addition to the consistency of the phase boundaries. An excellent shape memory effect and super-elasticity can be obtained only when all of the conditions are satisfied.

then, numerous research results have been disclosed, and more than a dozen alloys having the shape memory effect have been discovered.

However, when this effect was discovered in Ni-Ti alloys, the fact that these alloys have super-elasticity was not known. Therefore, super-elasticity has mainly been studied in Cu-Al-Ni alloys as a phenomenon which is independent from the shape memory effect. The super-elasticity of the Ni-Ti alloys was discovered at the beginning of the 1970s, immediately before it was clarified that the two phenomena depend upon super-elastic M-transformation.[11) 12)]

Materials which have corrosion and abrasion resistances in the high temperature phase have been developed for structural materials, completely independently of their shape memory effects as functional materials. These materials were realized as the functional materials much earlier.

3. Mechanisms of shape memory effect and super-elasticity.

The reasons governing the occurrence of the shape memory effect and super-elasticity are complicated, and not many details have been clarified scientifically. Therefore, only the mechanism which has been clarified will now be simply described (see Fig. 3).

When a shape memory alloy which is in an austenitic phase (abbreviated to A phase hereinafter) at a high temperature is cooled and the alloy passes a certain temperature (M-transformation start temperature, called the Ms point), the alloy M-transforms from the A phase to the M phase. The M phase is a well-known phenomenon which occurs when steels are rapidly cooled down. This phase also occurs in metals such as titanium or zirconium, or in alloys. This phenomenon is due to a phase transformation in which the crystal structure changes mainly by shear transformation, without any accompanying diffusion, with the solid phase thereof retained.[13)] When the M phase is heated to a temperature at which the M phase is returned back again to the A phase (This temperature is slightly higher than the Ms point reached during cooling, and is called the Af point. The previously described M-transformation temperature is this Af point.), the A phase is again realized. If no external force is applied, the

4. Application of shape memory Ni-Ti alloy

The firstly practical use of shape memory Ni-Ti alloys was

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realized by pipe joints.[14] An alloy of a low working temperature (approximately -150°C) is used for such a joint, and its inner diameter is slightly smaller than the outer diameter of the pipe. When pipes are to be connected, the joint is first immersed in liquid air and a plug is forced into the inside of the joint to expand its inner diameter. Then, as shown in Fig. 4, the pipes are inserted from both sides, then the joined pipes are left at room temperature until the diameter of the joint recovers to its pre-expansion dimensions. As a result, the pipes are clamped. More than 100,000 joints of this type are used in the hydraulic systems of F-14 jet fighters, and they have caused no problems such as oil leaks. Similar methods have been applied to various seals and clamps (Fig. 5 and Fig.6).

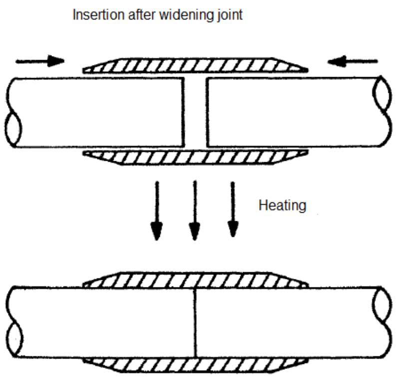

Fig. 4 Principle view of pipe joint using shape memory Ni-Ti alloy

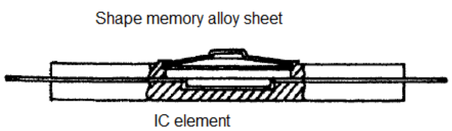

Fig. 5 Sealing of package of IC device using shape memory Alloy

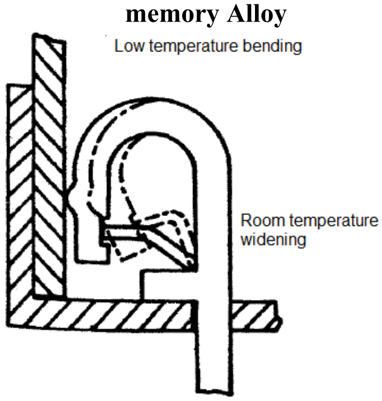

Fig. 6 Clamp made of shape memory Ni-Ti alloy

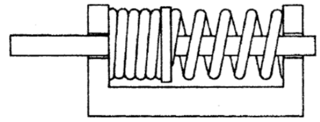

Fig. 7 Operational principles of two-way shape memory device in bias spring

Since Ni-Ti alloys do not react with organic substances, it is expected that they will be used in implants in living tissues. One application which is being widely studied is a bone setting plate that is used to provide internal bone setting in which a broken bone is fixed not by plaster but by bolts or the like. Methods of fixing intramedullary nails and base portions of artificial arthroses can also employ similar means. A method of curing scoliosis, in which a Ni-Ti alloy which retains the memory of a straight line is fixed in such a manner that the alloy is placed along the spine is then heated in order to straighten the spine, is a method which fully utilizes the characteristics of a shape memory alloy.

All of the shape memory effects mentioned above exhibit a phenomenon which is called the one-way effect. That is, when the alloy is heated after being deformed at a low temperature, the alloy recovers its shape once. Even if it is again cooled to the low temperature, it will not recover the shape it previous had when deformed at that low temperature. However, in general, a two-way device which repeatedly recovers is more advantageous from the functional view point, and its range of applications is wider than that of a one-way device. Therefore, various methods by which two-way characteristics can be provided for shape memory alloys have been studied. One such method involves the use of a bias force. This method utilizes the characteristic of a shape memory alloy that it is strong at high temperatures (where it is hard and has a high yield stress), but it is weak at low temperatures (where it is soft and has a low yield stress). For example, in a device in which a coil spring formed of a shape memory alloy and a normal coil spring are abutted against each other, as shown in Fig. 7, the shape memory alloy is pressed to the left at low temperature because the normal coil spring is stronger, while the shape memory alloy becomes stronger than the normal coil spring as temperature rises and forces it to the right.

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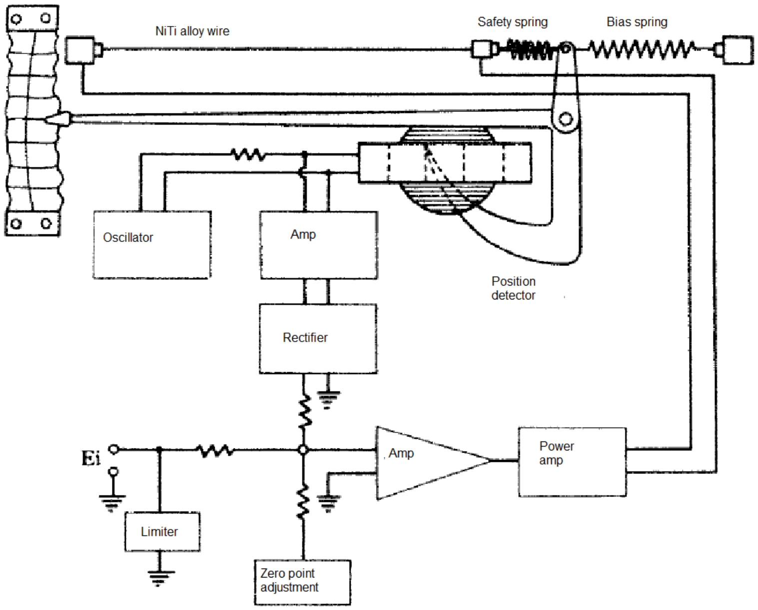

Fig. 8 Structure of actuating portion of pen recorder

A differential two-way device is well known as another type of the two-way device. This device utilizes the difference in force exerted by a shape memory alloy at high temperatures and low temperatures. For example, if shape memory alloys are used for both of the coils shown in Fig. 7, a differential two-way device is realized. When one of the coils is heated, the heated coil presses against the other coil to exert a force upon it. When the heating of the first coil is terminated and the other coil is heated, the coils move in the opposite directions.

A bimetal is well known as a two-way temperature detecting device. A shape memory device would be significantly superior to a bimetal because the shape memory device would be able to generate a large force, the shape change would occur rapidly at a specific temperature, and the magnitude of the change would be significantly large. In particular, the ability to generate a large force is the most important advantage for this type of device, because a single device has both a temperature detecting portion (sensor) and an actuating portion (actuator). It is important to consider that if a large device is used in order to obtain a large force, the actuation speed will inevitably become low because the actuating source is heat.

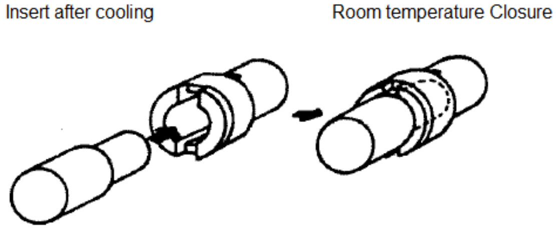

Fig. 9 Connector using shape memory alloy

Since Ni-Ti alloys have excellent corrosion resistances, a device of this type would have a very good resistance to the environment and the atmosphere except the temperature condition. Since the movable shaft sealing portions (seals) which are necessary in motors are not needed if a Ni-Ti alloy is used, these alloys are suitable for use in extreme environmental conditions or in places which are isolated from the atmosphere, and, in practice, applications in hard vacuum and nuclear reactors have been investigated.[15)]

The driving device of a pen recorder is an application of a two-way device. As shown in Fig. 8, the structure of the driving device is such that a straight Ni-Ti alloy wire is tensioned by a bias spring coil and a current is passed through it to heat it for operation. The pen recorder is designed so that the pen position is fed back so that no errors are generated by hysteresis or temperature changes.

Fig. 9 shows a connector[16)] which can be repeatedly used because it has a two-way operation, while the pipe joint described above which has a one-way action. A beryllium sleeve on the inside of the connector is provided with slits in such a way that the front end of the connector is opened in the free state. A ring of a Ni-Ti alloy, whose

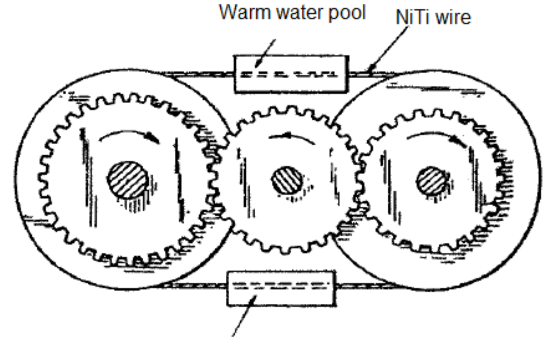

Fig. 10 Example of heat engine using shape memory effect of Ni-Ti alloy

actuating temperature is lower than room temperature, is installed around the sleeve. The front end is opened at low temperatures by the spring force of the sleeve, but at room temperature the ring recovers its shape so that the ring clamps a mating conductor. Spraying of gas is usually employed for obtaining the low temperature. Other two-way devices which have been disclosed include various thermal switches, circuit breakers and fire safety devices.

The use of shape memory alloys in automobiles has been

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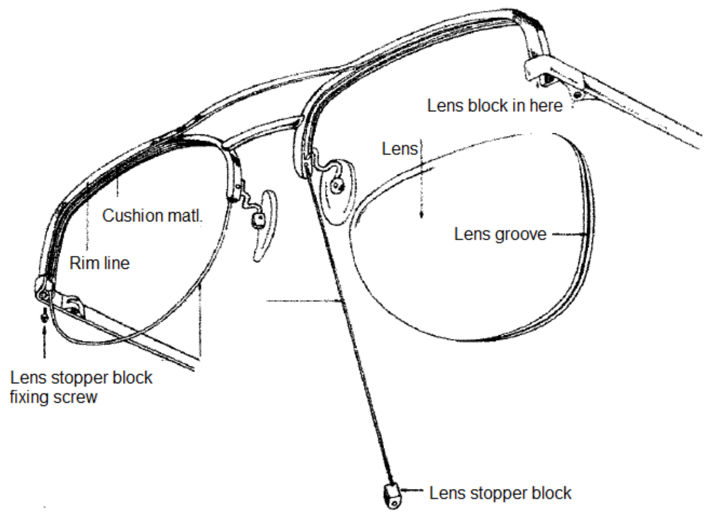
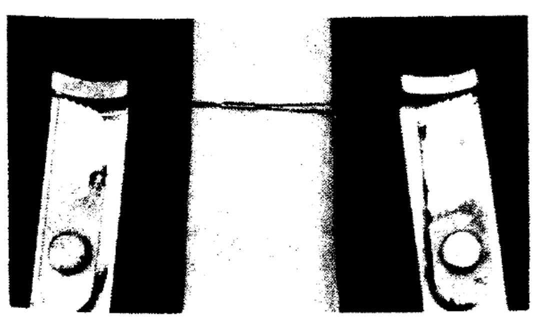


Fig. 11 Spectacle frame using super-elastic Ni-Ti wire

suggested, especially in radiator thermostats and fan clutches. A radiator thermostat is a device which cools engine cooling water by introducing the cooling water into the radiator only when the temperature of the cooling water rises. A fan clutch is a device which provides cooling by connecting a cooling fan to a rotary shaft when the engine reaches a predetermined temperature. Both devices were developed to reduce the warming-up time and save energy. Another proposed device is an injection nozzle of a carburetor which is designed to always provide the most suitable mixture ratio using a shape memory device which compensates for differences in the viscosity of gasoline at different temperatures.

Since differential shape memory devices can generate large forces and have high energy conversion ratios, they can not only be utilized in various actuators and manipulators for robots or the like, but they are also expected to be applied to heat engines in which mechanical energy is obtained from low grade energy sources such as exhaust heat (Fig. 10). Although such a heat engine has yet not been produced, it has been the subject of intense research, and a heat engine conference was held in the U.S. in 1978.[17)]



Photograph 2 Clamping of bone by super-elastic Ti-Ni alloy

5. Application of super-elastic Ni-Ti alloys

The first practical usage of super-elasticity is in the frames of spectacles.[18)] A Ni-Ti alloy is, as shown in figure 11, used as wire for fixing lenses. A conventional frame in which the lenses are suspended by wire made of a metal or synthetic resin, has the advantage of enabling a lightweight and a wide field of view, but it has the disadvantage that the lenses can easily fall out when they are wiped or when they contact at a temperature. The newly developed frame completely overcomes this problem, even if the lenses are strongly wiped or the temperature changes, by the use of an super-elastic wire for supporting the lenses.

Super-elastic Ni-Ti alloys are used in medical fields, in the same way as shape memory alloys. One application is in the correction of abnormal occlusion, that is, in the straightening of teeth. Although a full-band system which corrects abnormal occlusion by utilizing the elasticity of a wire is an excellent method, normal metal wires (made of stainless steel, Co-Cr alloy, or the like) have a poor range of elasticity, so the wire must be changed many times as the treatment progresses. If loops are made to increase the elastic range of the wire, the disadvantage arises that the patient feels discomfort. The use of a super-elastic wire can overcome these problems, and provide a great advantage, as can be expected from its stress-strain diagram, in that correcting force of the wire does not drop as the correction progresses. In order to use such characteristics, comprehensive research into improving the wire characteristics, fixing the wire to bone, and the most suitable shapes of arches or the like have been progressing.[19)] In the U.S, Ni-Ti alloy wires are used by nearly half the dentists for correcting abnormal occlusion. This method uses super-elastic characteristics and usages which are slightly different from those of basic super-elasticity, because the method is characterized in that the M phase of each Ni-Ti alloy is work-hardened to increase the elastic range.

Ni-Ti alloys are applied to methods of clamping bones in plastic surgery.[20)] In general, since living tissues automatically adjust to externally-applied loads, if a bone is strongly bound by stainless steel wire or the like, the tissues of the bone creep as they adjust to the load. Therefore, it is impossible to keep the bone clamped for a long period of time. If a super-elastic wire is used it can follow the contraction of the bone within its super-elastic range as the bone creeps, so that firm clamping can be maintained during the treatment. However, super-elastic wires have a problem. For example, such a wire cannot be fixed because it recovers its original form when an attempt is made to twist it by pliers, as if it was normal wire. This problem has been solved by caulking the wire after it has been passed through a thin pipe (photograph 2). This method of clamping has already been utilized clinically.

Since a super-elastic alloy has an excellent strain recovery ability

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which is an order of magnitude larger than those of normal materials for springs, it is of course expected to become a general-purpose material for springs. Furthermore, since a super-elastic spring is basically a non-linear spring, skillful use of this non-linearity will enable its use as a functional spring. However, such a spring does not exhibit any elastic strain, which will present some design problems. It will be difficult to obtain a relationship between load and displacement by using its rigidity and spring constant, and it will be difficult to simulate the strained state of the coil spring with the use of torsional moment because the large magnitude of the strain. In order to overcome these problems, research is under way into software which provides methods to design springs together with hardware techniques such as working methods and heat treatments.

Since super-elastic alloys have a damping ability caused by the hysteresis characteristics seen in their stress-strain curves in addition to the stress recovery ability, positive utilization of this feature in, for example, a contact spring which is able to prevent chattering, has been examined in the precision instrument field.

6. Conclusion

As described above, although the shape memory effect and super-elasticity of Ni-Ti alloys have been partially utilized, these efforts are still in the development stage. The hardware and software techniques required for realizing the utilization of these alloys have not yet been developed. However, since the unique feature of these alloys of being able to recover from strains of several percent raises strong demand for their use as functional materials, it is expected that they will be used in many fields.

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